

Set Of Reports And Articles Regarding Cement
Wastes Forms Containing Alpha Emitters That Are
Potentially Useful For Development Of Russian
Federation Waste Treatment Processes For
Solidification Of Weapons Plutonium MOX Fuel
Fabrication Wastes For Long-Term Storage And
Disposal

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This collection of Reports and Articles was put together to be provided to Russian experts at the US RF Experts Technical Meeting on: Management of Wastes from MOX Fuel Fabrication Facilities, in Moscow July 9-11, 2003.

June 12, 2003

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This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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This is a set of nine reports and articles that were kindly provided by Dr. Christine A. Langton from the Savannah River Site (SRS) to L. J. Jardine LLNL in June 2003. The reports discuss cement waste forms and primarily focus on gas generation in cement waste forms from alpha particle decays. However other items such as various cement compositions, cement product performance test results and some cement process parameters are also included.

This set of documents was put into this Lawrence Livermore National Laboratory (LLNL) releasable report for the sole purpose to provide a set of documents to Russian technical experts now beginning to study cement waste treatment processes for wastes from an excess weapons plutonium MOX fuel fabrication facility. The intent is to provide these reports for use at a US RF Experts Technical Meeting on: the Management of Wastes from MOX Fuel Fabrication Facilities, in Moscow July 9-11, 2003. The Russian experts should find these reports to be very useful for their technical and economic feasibility studies and the supporting R&D activities required to develop acceptable waste treatment processes for use in Russia as part of the ongoing Joint US RF Plutonium Disposition Activities.

Once again, this valuable set of reports is due to the efforts of Dr. Christine Langton from SRS and not anyone at LLNL.

L. Jardine

Listing of Reports and Articles Contained in This Document

1. Ned E. Bibler, Radiolytic Gas Generation in Concrete Made With Incinerator Ash Containing Transuranium Nuclides, Scientific Basis for Nuclear Waste Management, Vol. 2 pp. 585-592, book available from: Plenum Publishing Corporation, 1980.
2. V.W. Schneider and F.W. Ledebink, Cementation of TRU Waste by a New Process: Properties of the Products, Advances in Ceramics: Nuclear Waste Management I, eds. Wicks, G.G. and Ross, W.A., pp. 394-400, American Ceramic Society, 1984.
3. Ned E. Bibler, Gas Production From Alpha Radiolysis of Concrete Containing TRU Incinerator Ash, Progress Report 4, September 1, 1979-August 31, 1980, Publication Date: March 1981 (DPST-80-150-2)
4. David B. Barber, Gas Generation in Magnesium-Phosphate Cement Solids Incorporating Plutonium-Containing Ash Residue, Proceedings of the International Conference on Decommissioning and Decontamination and on Nuclear and Hazardous Waste Management Volume 1, pp. 458-466, September 13-18, 1998, Denver, Colorado, Published by: The American Nuclear Society, Inc.
5. Ned E. Bibler and Errol G. Orebaugh, Radiolytic Gas Production From Tritiated Waste Forms Gamma and Alpha Radiolysis Studies, Publication Date: 1977 (DP-1459).
6. Ned E. Bibler, Radiolytic Gas Production During Long-Term Storage of Nuclear Wastes, 28th Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tennessee, on October 27-29, 1976 (DP-MS-76-51).
7. J.A. Stone, Evaluation of Concrete as a Matrix For Solidification of Savannah River Plant Waste, Publication Date: June 1977 (DP-1448).
8. B.L. Anderson, M.K. Sheaffer, L.E. Fischer, Hydrogen Generation in TRU Waste Transportation Packages, Date Published: May 2000 (UCRL-ID-13852).
9. Christine A. Langton, Russian Grouting Experience (U), Report Date: May 13, 2002, (WSRC-TR-2002-00235, Revision 0) [V.A. Starchenko, NI. Alexandrov and V.P. Popik, The Review of the Russian Experience on Inorganic Binders for Waste Treatment and Tank Closures]

Reprinted from:

SCIENTIFIC BASIS FOR NUCLEAR WASTE MANAGEMENT, Vol. 2 (1980)
Edited by Clyde J.M. Northrup, Jr.
Book available from: Plenum Publishing Corporation
233 Spring Street, New York, N.Y. 10013

RADIOLYTIC GAS GENERATION IN CONCRETE MADE WITH
INCINERATOR ASH CONTAINING TRANSURANIUM NUCLIDES*

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ABSTRACT

The effects of various factors on H_2 generation by alpha radiolysis of concrete containing TRU incinerator ash were studied. Methods for reducing H_2 generation were investigated. Samples of portland and high-alumina cement containing up to 30% calcined ash (dry basis) were doped with $^{238}\text{PuO}_2$. Gas pressures were measured as a function of radiation dose; gas compositions were determined. Gas yields were calculated in terms of G values (molecules produced per 100 eV of alpha energy absorbed). These yields were used to estimate pressures in containers of radioactive concrete waste during storage.

INTRODUCTION

The action of α , β , or γ radiation of water produces hydrogen gas(1). Thus, nuclear waste forms, such as concrete, that contain H_2O can produce H_2 . Potentially, this can lead to pressurization of storage containers, or to the production of flammable or explosive gaseous mixtures.

This paper summarizes results of an extensive investigation (2) to estimate the rate of radiolytically generated H_2 evolution from concrete containing transuranium (TRU) waste. Other studies showed that $^{60}\text{Co}-\gamma$ and $^3\text{H}-\beta$ radiolysis of concrete also produce H_2 (3-5).

*Work done under USDOE Contract No. AT(07-2)-1.

The gas pressures generated during γ radiolysis of concrete reaches a low equilibrium value because of a back reaction between OH radicals and H_2 . Earlier studies (3,5) of alpha radiolysis of concrete showed that an equilibrium pressure was not attained at H_2 pressures up to 1.1 MPa indicating considerable H_2 accumulation in the container. The present study was initiated to estimate the radiolytic rate of gas production from concrete TRU incinerator ash during long term storage in the Waste Isolation Pilot Plant in New Mexico (6). The effects of various factors on this rate, along with methods to reduce it, were investigated.

EXPERIMENTAL PROCEDURE

Simulated TRU incinerator ash was prepared by calcining at 800°C the ash from impartial incineration of typical combustible laboratory wastes such as tissues or polyethylene tubing. Principal components of the ash were Ca (added as heat retardant to the plastics) and Ti (added as whitener). Carbon content of the calcined ash was nominally <1%.

Mixtures of 70 wt % cement [Portland Type I (P-1) or high-alumina (HAC)] and 30 wt % ash (dry basis) were prepared with a known amount of $^{238}\text{PuO}_2$. After thorough mixing, sufficient water was added to give a workable paste (initial water/cement = 0.8) which was then poured into a cylindrical steel mold (10 cm x 2 cm O.D.). After curing 5 to 30 days at ambient conditions, the final composition of the specimens (total weight = 60 g) was nominally 50 wt % cement, 20 wt % ash, and 30 wt % water containing 0.1 to 1.0 Ci of ^{238}Pu . In the presence of air, the specimen was sealed to a pressure transducer and the pressure increase recorded. After a known time, the gas was sampled and its composition determined by gas chromatography. G values (molecules produced/100 eV of α energy absorbed) were calculated from both the final gas composition and from the rate of pressure increase using the ideal gas law, the void volume in the container, and the amount of ^{238}Pu present.

GAS YIELDS

Typical pressure increases for three concretes are shown in Fig. 1. Sample P-1 and HAC-1 contained simulated ash doped with $^{238}\text{PuO}_2$, and sample HAC-2 contained ash prepared from incineration of waste contaminated with a ^{238}Pu solution. Thus, HAC-2 resembled more closely an actual waste form. These three samples were cured unsealed at ambient conditions for approximately a month. When non-radioactive concretes were sealed to the transducer, no pressure was produced, confirming that radiolysis caused the pressure increases.

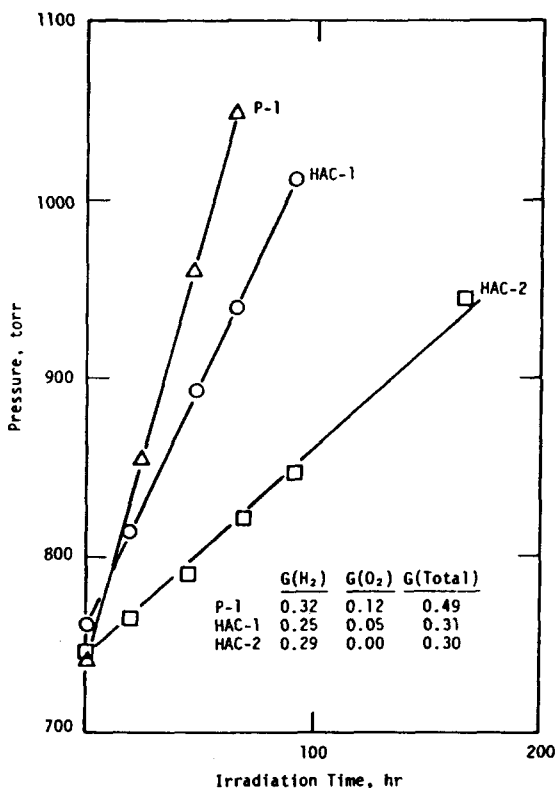


Fig. 1. Pressure Increase from Radiolysis of Portland or High Alumina Concrete Containing ^{238}Pu

The slopes of the three lines in Fig. 1. differ because of differences in the G values and dose rates for the three concretes. $G(H_2)$ and $G(O_2)$ values were calculated from the changes in the partial pressures of H_2 and O_2 during the test. The partial pressure of N_2 was unchanged by radiolysis. G (total) is the 100-eV yield of all gaseous molecules and was calculated from the slopes of the lines. Within experimental error, $G(H_2) + G(O_2) = G$ (total) as expected if the N_2 pressure is unchanged. Less than a stoichiometric amount of O_2 was formed, as indicated by the ratio $G(O_2)/G(H_2)$ being less than 0.5 (Fig. 1). This agrees with the α radiolysis of liquid water where $G(O_2)/G(H_2)$ is only 0.13 (7). The reason for O_2 not being produced with HAC-2 at this time is unknown. Less than a stoichiometric amount of O_2 being formed indicates that some other oxidation product of water is being formed. Perhaps this is H_2O_2 as it is in liquid water. Another study showed evidence of this species in γ irradiated concrete (3).

Dose rates for the tests shown in Fig. 1. were nominally 10^{17} eV/(min) (gram of concrete), with HAC-2 having the lowest rate. This dose rate is about 1000 times larger than that expected in actual waste. For example, the dose rate in a 210-liter drum 90% full of concrete containing 200 g ^{239}Pu is only 4×10^{14} eV/(min) (gram of concrete). If H_2 is formed as it is in liquid water (recombination of H atoms or hydrated electrons), no change in $G(\text{H}_2)$ at lower dose rates is predicted and none was observed over dose rates of 10^{16} to 10^{17} eV/(min) (gram of concrete). Over the range 23 to 100°C , $G(\text{H}_2)$ is independent of temperature for concretes containing the same amount of water. This agrees with the radiolysis of liquid H_2O where $G(\text{H}_2)$ is not significantly affected by temperature (1).

REDUCTION OF $G(\text{H}_2)$

Lower rates of H_2 production would be desirable both for short and long term considerations. Two methods were found to reduce $G(\text{H}_2)$: 1) addition of H atom scavengers to concrete, 2) removal of H_2O by heating concrete or using pressed concrete. The latter method would be effective over the long term only if water were excluded from the concrete during storage. The best H atom scavengers for reducing $G(\text{H}_2)$ were NO_3^- and NO_2^- . These were supplied by adding NaNO_3 and NaNO_2 to the water used to make the concrete. Maximum concentrations of these ions in the solutions were 6M for NO_3^- and 5M for NO_2^- . $G(\text{H}_2)$ with NO_3^- was reduced to 0.03. $G(\text{H}_2)$ with NO_2^- was reduced to 0.053.

Radiolysis caused O_2 production in the presence of NO_3^- ($G=0.37$) and O_2 consumption in the presence of NO_2^- ($G = -0.08$). Also, when NO_2^- was present, a slight amount of N_2O was produced [$G(\text{N}_2\text{O}) = 0.04$] indicating reduction of the NO_2^- . Relative decreases in $G(\text{H}_2)$ upon addition of NO_3^- or NO_2^- ions are shown in Fig. 2. The data for NO_3^- ions follow the trend shown by the solid line which depicts the effect of these ions in the γ radiolysis of liquid water (7). This similarity indicates that these ions are reacting as they do in liquid water. Further, this suggests that the reaction for H_2 formation from α radiolysis of concrete may be identical to that for liquid water. The effect of NO_2^- ions on $G(\text{H}_2)$ from α radiolysis of liquid water has not been determined.

One method of obtaining a concrete with low water content is to prepare a pressed concrete. This concrete is prepared by pressing a cement-ash pellet containing very little water (about 2 wt %), at 173 MPa (8). Gas production from three pressed concretes containing portland Type I cement doped with $^{238}\text{PuO}_2$ was measured. Two concretes contained simulated TRU incinerator ash. The third contained bone char (a material for absorbing Pu from waste streams). $G(\text{H}_2)$ values measured from the amount of H_2 produced were 0.009 and 0.005 for the concretes containing ash and 0.003 for the one containing

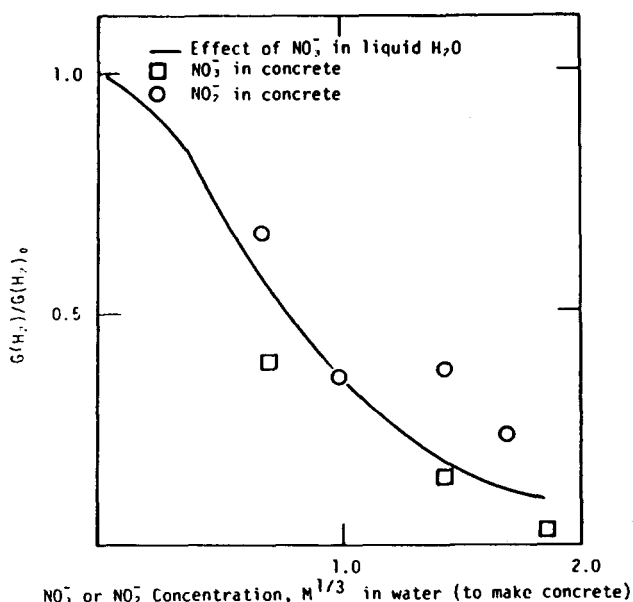


Fig. 2. Lowering of $G(\text{H}_2)$ in α Radiolysis of Concrete by Addition of NO_3^- or NO_2^- Ions

bone char. Pressure increases were insufficient to calculate values for $G(\text{total})$ because of the relative large void volumes of the containers. To determine the consequence of this type of concrete becoming wet, pressure measurements were made while a pressed concrete containing ash was submerged in water. $G(\text{H}_2)$ increased to 0.13. O_2 was produced [$G(\text{O}_2) = 0.03$] and $G(\text{total})$ was 0.16. Weight measurements indicated that the sample had sorbed 16 wt % H_2O . Clearly, to retain the low rate of H_2 production, water must be excluded from the concrete during storage.

Another method of reducing the water content is to heat the concrete to remove free water after the concrete has cured for a sufficient time. Most of the H_2O in concrete is added to achieve a workable paste that can be poured or cast rather than to cause the hydration reactions that give concrete its strength (9). The drastic reduction in the pressurization rate caused by prior heating at 200°C to remove H_2O is shown in Fig. 3. Heating at 90°C did reduce the G values, but not as significantly as heating at 200°C . The concrete used to obtain the results in Fig. 3. has been cured at room temperature in a moist environment for 36 days before it was heated and thus had attained at least 70% of its final strength. It was dried by heating in an oven in the steel cylinder into which it was cast. At 90°C , the sample showed a continuous weight loss as long as it was heated (34 hr). At 200°C weight loss had ceased after 16 hours of

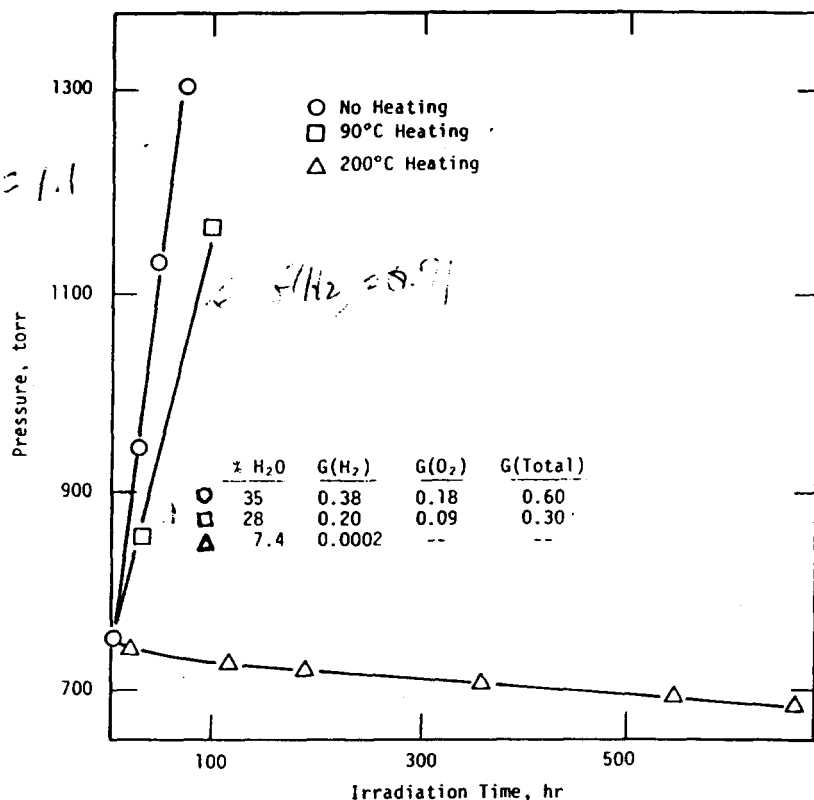


Fig. 3. Pressure from Alpha Radiolysis of a Previously Heated Portland Concrete Waste Form

heating. In both tests, the temperature of the concrete had returned to ambient before the sample was sealed to the transducer.

A very low value for $G(H_2)$ was obtained for the concrete that has been heated to 200°C. Low $G(H_2)$ values were also found for other concretes after they had been heated at 200°C. For HAC-2 (Fig. 1.) and for a pressed concrete, $G(H_2)$ values of 5×10^{-4} and 3×10^{-4} , respectively, were obtained. The pressure above these samples also decreased when they were sealed to pressure transducers. A pressure decrease was also observed after a nonradioactive concrete after it has been heated to 200°C.

The results in Fig. 3. indicate that the water driven off concrete at temperatures below 200°C is radiolytically reduced more easily than the remaining water. The remaining water is probably involved in the hydration reactions that give the concrete its strength. When water was again added to the concrete used to obtain

the data in Fig. 3., $G(H_2)$ and $G(O_2)$ increased to nearly their original values, 0.34 and 0.18, respectively.

RADIOLYTIC PRESSURES IN STORAGE CONTAINERS

The above G values can be used to calculate pressures generated by radiolysis in a storage container of concrete containing TRU waste. The equation for a concrete containing several TRU isotopes is:

$$P = \frac{[1.2 \times 10^{18} \alpha/(\text{year})(Ci)] [G(\text{total})] RT}{100 \text{ NV}} \sum_i \frac{Ci_i E_i (1 - e^{-\lambda_i t})}{\lambda_i}$$

where Ci_i , E_i , and λ_i are the number of curies, the α energy, and the α decay constant, respectively of the i -th isotope. Pressures for H_2 and O_2 can also be calculated using $G(H_2)$ or $G(O_2)$. Results for H_2 generation in a 210-liter container 90% full of concrete (10% porosity) containing 200 g of ^{239}Pu are shown for various values of $G(H_2)$ in Fig. 4. The lines were calculated by assuming the $G(H_2)$ was not affected by the H_2 pressure and that a slow thermal recombination reaction of H_2 and O_2 was not occurring over the long storage times. A previous α -radiolysis test has shown that $G(H_2)$ is not significantly affected by H_2 pressures up to 1.1 MPa (3). Also, no evidence for a thermally induced recombination reaction has been observed at the α dose rates used thus far.

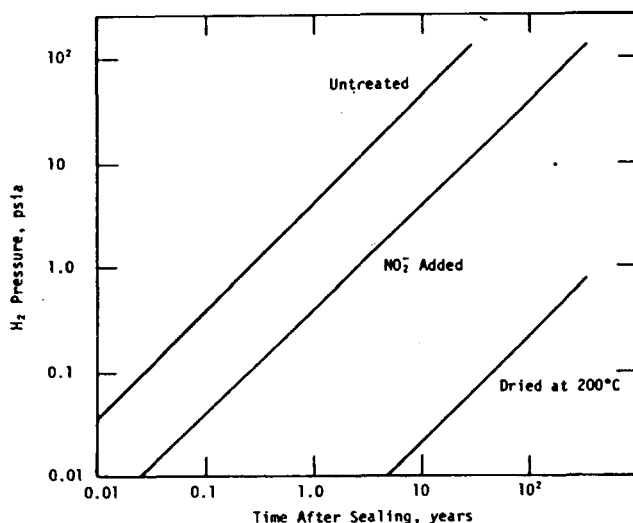


Fig. 4. Calculated Radiolytic H_2 Pressure in a 210-liter Container 90% full of Portland Concrete and 200 g ^{239}Pu

The effect of adding NO_2^- to the concrete or of drying the concrete is clearly evident in Fig. 4. With untreated concrete, considerable H_2 pressures can be generated after intermediate storage times. Also, with the untreated concrete, a flammable mixture (4% H_2 in air) can be present after only about 40 days. With concrete dried at 200°C more than 10^2 years would be necessary to generate a flammable mixture. If less ^{239}Pu is present, longer times would be necessary.

CONCLUSIONS

H_2 and O_2 will be produced by a radiolysis during storage of canisters of portland or high alumina concrete containing TRU waste. The rate of H_2 production can be decreased by adding NO_3^- or NO_2^- ions to the concrete or by drying the concrete. NO_3^- addition increases O_2 production while NO_2^- addition decreases O_2 production. Drying at 200°C reduces the rate of H_2 production by a factor of approximately 2000 while reducing the water content by a factor of only 5. If H_2O is again added to the concrete, the gas production rates return to nearly their original values.

REFERENCES

1. I. G. Draganic' and Z. D. Draganic', The Radiation Chemistry of Water (Academic Press, New York, 1971).
2. N. E. Bibler, USDOE Report DPST-78-150-2, Du Pont Company (1979).
3. N. E. Bibler, USDOE Report DP-1464, Du Pont Company (1978).
4. W. E. Tadlock and G. C. Asbell, USDOE Report MLM-2620, Tritium Waste Controls, October-March 1979 (1979).
5. N. E. Bibler and E. G. Orebaugh, USDOE Report DP-1459, Du Pont Company (1977).
6. M. A. Molecke, Trans. Amer. Nucl. Soc. 27, 440 (1978).
7. N. E. Bibler, J. Phys. Chem. 78, 211 (1974).
8. L. M. Klinger, D. H. Batchelder, and E. L. Lewis, USDOE Report MLM-2575 (1978).
9. F. M. Lea, The Chemistry of Cement and Concrete, 3rd Ed. (Chemical Publishing Company, New York, 1971).

Cementation of TRU waste by a new process: Properties of the products

(2)

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The background for selection of a process to solidify the waste arising from the fabrication of MOX fuel is provided. Cement has many advantages as a matrix for TRU waste. Improvements of the cementation process make it possible to include all types of waste in only one product. A process description is followed by a detailed presentation of the product and its properties. Finally, properties are outlined which may be subject to quality control.

During plutonium mixed oxide (MOX) fuel fabrication a small, but unavoidable, amount of α -bearing [transuranic (TRU)] waste is formed. The second line of Fig. 1 categorizes 4 main classes of waste according to source and nature. There are wastes arising in the glove boxes which are caused by operation steps (solid box waste) or replacement of equipment (retired equipment); others are generated by the processes themselves as filtrates from conversion or liquids from analytical procedures (liquid box waste). Waste from outside the glove box but inside the working area ("room waste") is suspected of being contaminated and therefore handled as active waste, although it is usually free from plutonium. It is worthwhile keeping this waste separate from the box waste.

Before these wastes can be disposed of, they have to be treated to meet legal requirements set up by licensed authorities and the operators of the disposal site.

When selecting an appropriate process which had to fulfill those requirements as well as to meet the needs of a mixed oxide fuel fabrication plant (MOFFP), we had to bear in mind a number of conditions. The process chosen should be easy to operate, with a few process steps and high reliability. The process should be capable of handling all of the different waste streams shown in the second line of Fig. 1. According to German regulations, all the wastes should be solidified. Currently, all TRU waste is buried in deep geological repositories in the Federal Republic of Germany. No shallow land burial is planned. Therefore, there is no incentive to separate primary wastes into categories according to α activity.

Process selection

Many different methods for immobilization of wastes have been suggested to date. Ross et al.¹ have recently summarized the major advantages and disadvantages of a number of immobilization systems. They concluded that "each system has its own inherent considerations. An evaluation of these considerations suggests the implementation of a cement or glass system."

The various processing techniques to immobilize wastes by cement are simple to use, less costly compared to other processes, and based on a large amount of

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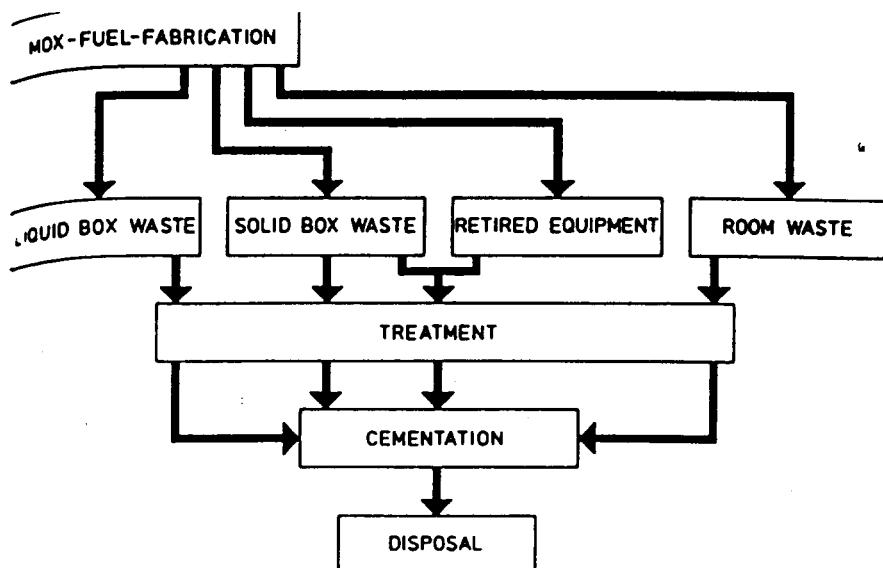


Fig. 1. Scheme for treatment of TRU waste arising from the fabrication of MOX fuel.

conventional experience. Operations are generally carried out at low temperature and thus avoid the risks of fire.

During its solidification and during its contacts with water, cement provides an alkaline environment. This offers an additional advantage, because plutonium which is not present as insoluble PuO_2 forms the very insoluble $\text{Pu}(\text{OH})_4$. It is therefore understandable that the leach rates for plutonium immobilized in cement are reported to be very low.^{1,2} We have therefore considered ways that the four waste streams shown in Fig. 1 could be combined and solidified by a simple cementation process.

As about 50% of the solid glove-box waste is combustible, incineration is often suggested for volume reduction. However, with the high percentage of PVC and neoprene in this waste, a large volume of contaminated secondary wastes (NaCl from off-gas scrubbing) is produced along with the ash. If these secondary wastes cannot be disposed of in a more simplified way, the process loses much of its interest.

On the other hand, we knew that while others had found materials such as gloves and plastic foils unstable and heterogeneous when solidified in cement, we overcame this difficulty by shredding all the soft material to particles <5 mm in diameter.

Process description

The wastes are segregated according to nature and composition upon entering the waste facility. Wastes worthwhile of Pu recovery (about 20%) first undergo washing processes³ and are then fed into the main streams of solid box waste and retired equipment. The soft materials of these streams are sent to a shredder (conventional type adapted for glove-box use) which cuts about 80 kg/h of waste

into particles <5-mm diameter. The shredded material is pneumatically transferred to a cyclone above the cement blender, where the waste can be homogenized.

In the cementation unit (a conventional, continuously working screw feeder type), the shredded soft waste is blended with cement and the liquid waste stream which has been treated for Pu recovery before. The flow of all three materials can be regulated separately, thus meeting the process parameters. This process control is part of the quality assurance of the product.

This blend of cement liquid and solid (soft) waste is poured directly into a 0.21-m³ (55-gal) drum over the pieces of hard solid waste.

Product

The product resulting from the above process is a package consisting of a 0.21-m³ drum filled with a homogeneous cement block which is reinforced by stainless steel (most of the hard solid waste is stainless steel). The drum is filled to about 95% (0.2 m³). Table I gives an example of a typical composition. In practice the plutonium amount will be about 15 g/0.21-m³ drum.

We used blast furnace cement because it showed the best resistance against corrosion in saturated brines. A cement liquefier and stabilizer are added to keep the water/cement ratio down (0.4 or even lower) without affecting flowability.

Table I. Typical composition of the immobilized TRU waste in a 0.21-m³ drum

Item	Quantity (kg)	Volume (dm ³)
Cement	200	65
Liquid waste containing sodium nitrate	80 } 20 }	87
Soft solid waste	40	32
Hard solid waste	60	10
Porosity, 3%		6
Final cement product	400	200

Properties of the package and cement product

The properties needed for safe disposal of the waste are different, depending on whether the repository is open and being operated or whether the repository is closed. In the case of a closed deep geologic repository the geology will provide the final and most important barrier so that additional engineered barriers around the TRU waste will not reduce any leak of activity very much. Such barriers therefore have their importance mainly for the operations before closing the repository.

Some of the properties are expected to show a dependence on the composition of the conditioned waste. We therefore carefully investigated the dependence of the properties of our product on the type of cement and the proportions of the different components. This allowed us to optimize the product and also have a broader understanding about the reliability of the process. It turns out that the properties of the package and cement product as reported below are not limited to the figure in Table I but represent a wide range of composition. This provides sufficient room for process deviations and normal waste composition variations.

Surface dose rate and surface contamination

The surface dose rate ($<10^{-4}$ Sv/h [<10 mrem/h]) will be far below the required threshold value (2×10^{-3} Sv/h). Also, the limit of the surface contamination required can be met. The mild steel drums are protected against corrosion by an epoxy resin coating of 150- μ m thickness and are therefore expected to survive undamaged for an intermediate storage time of several decades. The epoxy resin coating also allows the drums to be easily decontaminated.

Compressive strength

The compressive strength was studied as a function of the portion of soft waste in the product and the water/cement ratio. As a result it can be stated that the compressive strength of the product as given in Table I is about 20 N/mm² which is much higher than the present minimum need. The stocking of the filled drums also has to be considered in this connection.

Radiolysis gas generation

This phenomenon was investigated with a number of 1-dm³ samples, each corresponding to the standard product with the exception of salt content (Pu content, content of soft solid waste, water/cement ratio, but not sodium nitrate); in half of the samples the Pu was added as PuO₂ and in the second half as Pu solution. It was found that about 1.6 L of H₂/Ci_a·year in the case of PuO₂ and 2 L of H₂/Ci_a·year in the case of the solute plutonium are generated. Oxygen was not generated; on the contrary, the oxygen in the gas phase (air) above the samples was removed, resulting in an underpressure corresponding to the portion of oxygen in air. The results are in good agreement with values reported by Kosiewicz.⁴ The investigations will be continued in two directions: leakage rate for H₂ of the drums to avoid overpressure in the package and addition of nitrate or nitrite which will reduce H₂ generation up to a factor of 50, according to Bibler.⁵

Behavior in case of incidents

Drop tests: Three types of experiments were conducted in which four packages were stacked up and the top drum made to fall onto the steel-covered concrete floor. The first experiment used drums filled to not more than 95%, with the mushroom-shaped lid kept empty. The packages remained tight after the drop, still having the underpressure caused by the setting. Even the cement product was nearly undamaged. The second used a package as before, but this was dropped onto another full package lying on the floor instead of the steel plate. The result was the same as above for both packages. The third used drums completely filled, with no voids. Here the drum broke open a few centimeters up near the flange, but only about 10 g of the product leaked out.

These results show that the container when exposed to mechanical power as might occur by maloperation during transportation or storage will remain tight, or, failing, the amount of activity released will be very limited.

Fire tests: A filled drum was placed into an isopropyl alcohol fire for one-half hour. The temperature measured in the gap between the drum and the product was 100°C; 50 mm inside the block the temperature was 90°C, and 100 mm inside the block it was 40°C. The gasket of the lid was destroyed and white steam escaped from the drum. The loss of weight was 15 kg (about 3.8%) compared to 10–12 kg in the case of cement product without the organic waste component. The organic waste was affected up to 5 mm depth. We intend to repeat these experiments with cesium-doped cement waste product in order to investigate the activity release more quantitatively.

Table II. Corrosion tests with blast furnace cement product at 90°C (2×2×8-cm³ samples containing 10% soft waste with a water-cement ratio of 0.40)

Media	Bending strength (N/mm ²)	Compressive strength (N/mm ²)
Damp room	3.8	17.6
Brine	4.2	15.0
Sodium chloride	3.8	13.0
Water	2.0	11.8

Table III. Corrosion test with blast furnace cement product at 55°C for 365 days (2×2×8-cm³ samples containing 10% soft waste, 0.3% liquefier, 0.5% stabilizer, with a cement-water ratio of 0.43)

Time (days)	Damp room		Water		Brine (Q type)	
	Bend. strength (N/mm ²)	Compr. strength (N/mm ²)	Bend. strength (N/mm ²)	Compr. strength (N/mm ²)	Bend. strength (N/mm ²)	Compr. strength (N/mm ²)
56	7	28.7	4.3	17.4	7.1	23.2
112	6.8	35.4	3.7	22.3	4.8	24.2

Corrosion resistance

Corrosion tests have been performed in order to find the most adequate type of cement. Water and brine (Q type) have been used as leachants. The corrosion attack was determined on the basis of changes at 90°C in the bending and compressive strength. Table II shows the results for blast furnace cement, which was better than the other 5 candidates under the conditions of this "quick" test. Tables II and III show a very good resistance against corrosion. One should not compare the figures of both tables with each other. The samples in Table III have been prepared with a high-speed lab blender which produced a higher porosity and therefore lower strength. Therefore, the data in the two tables should not be compared.

Leachability

Investigations of the leachability of the product are still going on. Three types of prisms (about 2×2×8 cm) are being leached in stagnant brine following the ISO norm: (1) cement product containing 10% soft waste contaminated with PuO₂, (2) same as (1) but without the soft waste, and (3) same as (1) but with Pu(OH)₃ instead of PuO₂ as contaminant.

Our conclusion from Fig. 2, which shows results obtained up to now, is that at the very beginning some activity is leached from the surface of the bodies which later disappears from the solution either by precipitation or by resorption on the surface of the cement body. We expect that the cement surface gets coated by a layer of magnesium hydroxide when exposed to the brine.

The experiments will be continued. Additionally, the behavior of crushed cement products are being investigated to simulate the case where the monolithic block was disintegrated after being in brine for centuries. For this purpose prisms as described above are crushed in a mortar. Preliminary results show that this procedure will change the values in Fig. 2 only by a factor of 10.

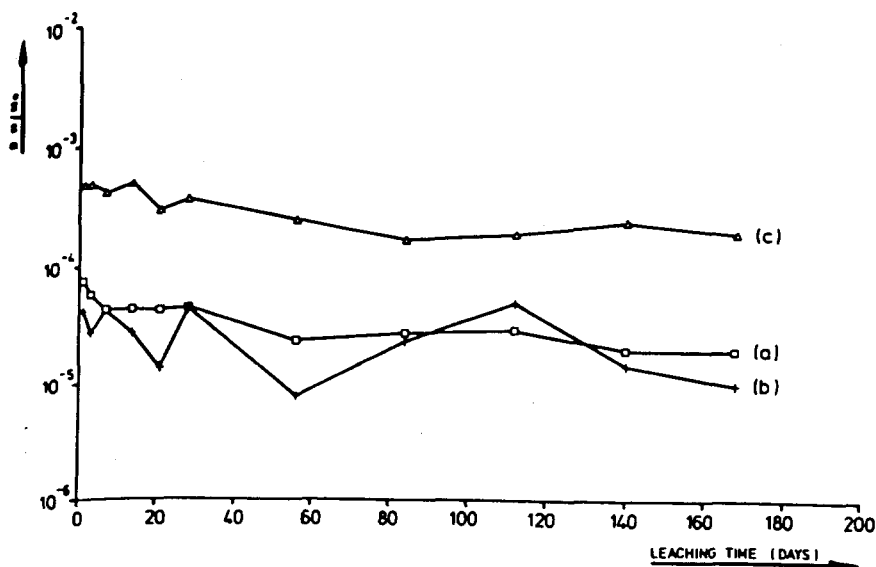


Fig. 2. Cumulative leached plutonium fractions.

Quality control

The quality control to which parameters and properties of radioactive waste conditioned for disposal have to be subjected has not been finalized. There is a broad common understanding that destructive controls on the final products should be avoided. The quality control therefore will concentrate on process control procedures and nondestructive product controls. Table IV shows the properties which are currently envisioned as being controlled. There is no difficulty in adapting this system of quality control to the process or product as described in this paper.

Conclusion

The process meets all the desired standards for a solidification process for TRU waste. It is easy to operate and, because conventionally proven, highly

Table IV. Properties subject to quality control

Inventory of activities
Dose rate
Surface contamination
Chemical composition of primary waste
Quality of the cement
Quality of the container
Ratio waste/cement/water
Degree of homogeneity
Weight
No free liquid

reliable. The properties of the conditioned waste as assured by process control meet the requirements.

It is often argued that adding cement would mean an undesirable increase of the waste volume. Here we can state a very unexpected result. Table V illustrates that a volume reduction of 40% can be achieved when wastes originally tightly packed but not compressed from the plant are processed as discussed in this paper.

Table V. Comparison of waste loadings for a 0.21-m³ drum

Material	Primary waste (kg)	Immobilized waste (kg)
Soft solid waste	24	40
Hard solid waste	36	60
Total	60	100

Acknowledgment

The authors thank H. Brunner (NUKEM GmbH, Hanau) for his excellent collaboration when investigating the product properties and assistance in preparing this paper.

References

- ¹W.A. Ross et al.; A Comparative Assessment of TRU Waste Forms and Processes. Vol. I and II, PNL-4428. Pacific Northwest Laboratory, Richland, WA, 1982.
- ²R. Neilson and P. Colombo, "Plutonium Leachability from Alternative TRU-Incinerator Ash Waste Forms," IAEA-SN-246/45, International Atomic Energy Agency, Vienna, Austria.
- ³V.W. Schneider and F.W. Ledebink, "Treatment of TRU-Wastes Recent Results of Developments Underway in Germany"; p. 362 in Proceedings of ANS Topical Meeting on Treatment and Handling of Radioactive Wastes, Richland, WA, 1982.
- ⁴St. T. Kosiewicz, "Gas Generation from Organic TRU-Wastes," *Nucl. Technol.*, 54, 92 (1981).
- ⁵N.E. Bibler, "Radiolytic Gas Generation in Concrete Made with Incinerator Ash Containing Transuranic Nuclides," DP-MS-79-25, presented at the Symposium on the Scientific Basis for Nuclear Waste Management, Boston, MA, 1979.

GAS PRODUCTION FROM ALPHA RADIOLYSIS OF CONCRETE CONTAINING TRU INCINERATOR ASH

PROGRESS REPORT 4
SEPTEMBER 1, 1979 — AUGUST 31, 1980

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PREPARED FOR THE U. S. DEPARTMENT OF ENERGY UNDER CONTRACT DE-AC0576SR00001

DPST-80-150-2

**GAS PRODUCTION FROM ALPHA
RADIOLYSIS OF CONCRETE CONTAINING
TRU INCINERATOR ASH**

**PROGRESS REPORT 4
SEPTEMBER 1, 1979 — AUGUST 31, 1980**

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Publication Date: March 1981

ABSTRACT

This report describes work performed from September 1, 1979, to February 29, 1980, in an experimental program to measure H_2 production from alpha radiolysis of concrete. Concrete is a candidate material for solidification of radioactive ash from incineration of solid wastes contaminated with transuranic isotopes. Tests described here were performed with concrete and simulated ash doped with Pu-238. The Pu-238 was added as solid PuO_2 or as plutonium dissolved in dilute H_2SO_4 . Two tests are described in this report. First is a test with portland Type I concrete to determine if high H_2 pressures affect the rate of H_2 production $[G(H_2)]$ in alpha radiolysis as they do in gamma radiolysis. Preliminary results indicate that both H_2 and O_2 are produced (H_2/O_2 = about 2) from the water decomposition and that H_2 pressures up to 130 psi do not significantly affect $G(H_2)$. A value of 15 percent was calculated for the porosity of the concrete from this test. An accurate value of this factor is necessary to calculate pressures generated by radiolysis in waste containers of concrete. The second test described in this report involves two long-term experiments with portland Type I concrete and high-alumina concrete at a low dose rate. Comparison with earlier results confirms that no dose rate effect on $G(H_2)$ exists for either type in the range 4×10^{15} to 1×10^{17} eV/min per gram of concrete. This suggests that lower dose rates will not affect $G(H_2)$.

FOREWORD

Previous reports in the program, of which this report is a part, are:

- DP-MS-79-25 (Summary paper presented to the 2nd International Symposium on the Scientific Basis for Nuclear Waste Management)
- DPST-78-150-1 (Presents work performed during April-July 31, 1978)
- DPST-78-150-2 (Presents work performed during August 1-November 30, 1978)
- DPST-80-150-1 (Presents work performed during December 1, 1978-August 31, 1979)

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GAS PRODUCTION FROM ALPHA RADIOLYSIS OF CONCRETE CONTAINING TRU INCINERATOR ASH

INTRODUCTION

Concrete is being considered as a solidification matrix for transuranic (TRU) radioactive waste ash. Primarily, this waste will be laboratory waste that will be incinerated for volume reduction. Because of the alpha radiation in the TRU waste, H_2 gas can be formed from radiolytic decomposition of the contained H_2O . Production of H_2 could be a potential hazard because of its flammability and because of a possible long-term buildup of pressure in a radioactive waste canister or sealed repository.

In this program, sponsored by the Waste Isolation Pilot Plant (WIPP) Project of Sandia National Laboratories, Savannah River Laboratory (SRL) is measuring gas production rates from concrete that contains plutonium-contaminated simulated TRU ash. SRL is also investigating methods for reducing H_2 production.

This report is the fourth in the program and presents results obtained from September 1, 1979, to February 29, 1980. Earlier results are summarized in a paper¹ presented to the Materials Research Society in November 1979. Also, other reports on the work in detail^{2,3,4} and on the production of H_2 from concrete by radiolysis by ^{60}Co gamma rays^{5,6} and H-3 beta particles⁷ have been published.

Previous work¹⁻³ has established that radiolysis of the concrete by alpha particles from the TRU isotopes produces both H_2 and O_2 by decomposition of the water. The rate, in terms of molecules per 100 eV of alpha energy absorbed (G value), is somewhat lower for concrete made from high-alumina cement than for concrete made from portland Type I cement. The effective G values in both types of concrete can be lowered by removal of the free water* from the concrete or by addition to the concrete of solutes such as $NaNO_3$ or $NaNO_2$ that scavenge the precursors of H_2 . The earlier tests also showed that below 100°C (the maximum temperatures tested) the H_2 production rate (molecules/100 eV) is independent of temperature and the radiation dose rate. Dose rates

* Free water is that water not used in the hydration reactions of the cement.

where

$\Delta P/\Delta t$ = rate of pressure increase, psi/hr

N = Avogadro's number

V = Gas volume, mL

R = ideal gas constant, 1.2×10^3 (psi)(mL)/(mole)(°K)

T = temperature, °K

$\Delta D/\Delta t$ = dose rate, eV/(hr)

Dose rates per unit mass could be calculated from the curies of Pu-238 present, the energy of the alpha particles, and the mass of concrete in the sample.

$$\frac{\Delta D}{\Delta t} = \frac{AE\alpha Ci}{M} \quad (2)$$

where

A = activity = $[3.7 \times 10^{10} \text{ dis}/(\text{sec})(\text{Ci})][60 \text{ sec}/\text{min}]$
= $2.2 \times 10^{12} \text{ dis}/(\text{min})(\text{Ci})$ for any radionuclide

E_α = energy of alpha particle
= $5.49 \times 10^6 \text{ eV}/\alpha$ for Pu-238

Ci = curies of Pu-238 present in concrete

M = mass of concrete (cement + water + ash), grams

Second, G values for the production or depletion of individual gases, $G(i)$, were calculated from the total dose and the composition of the gas mixture at the end of each test:

$$G(i) = \Delta P(i) \cdot \frac{NV}{RT} \cdot \frac{100}{D} \quad (3)$$

where

$P(i)$ = pressure change for gas i

D = total dose to the sample = $(\Delta D/\Delta t) \cdot t$

The final pressure of gas i was calculated from the final total pressure and the fraction of gas i in the final gas mixture. This fraction was determined by gas chromatography.

Apparatus for the High Pressure Test

The high pressure test is being conducted in a Parr bomb reaction vessel* capable of withstanding a pressure of 4500 psig. Attached to the bomb is a rupture disc rated at 3000 psig and a 0-2500 psig sputtered gage pressure transducer** capable of withstanding 7500 psig. The reaction vessel was completely filled with the concrete mixture (474 mL). Total free volume in the transducer, rupture disc, and connecting valve to the transducer is only 4.5 mL.

Calibration of the transducer was checked by hydrostatic testing. The output was linear with pressure (Figure 3). The sensitivity was 30.9 mV for 2500 psig. This value agreed within 0.6 percent of that cited by the manufacturer. The long-term performance stability of the transducer is rated at $\pm 0.1\%$ by the manufacturer.

Sample Preparation for the High Pressure Test

Weighed amounts of portland Type I cement and calcined ash were mixed and placed in the glove box. A weighed amount of PuO_2 containing Pu-238 was then mixed into the dry mix. A weighed amount of water was added and a paste made. A 474 mL and a 10 mL container were then filled with the paste. The mixing vessel and the small container were weighed so that the amount of paste added to each container could be calculated. A balance suitable for weighing the concrete in the large container was not available in the glove box. After the samples had cured one day, the samples were sealed to the pressure transducer. The smaller container had a 0 to 50 psi transducer. Final compositions of the samples and the void volume in the smaller container are given in Table 2.

Calculation of the Porosity of the Ash-Concrete from High Pressure Data

The volume available to the gas in the high pressure test can be calculated from the initial rate of gas production and the dose rate in that test along with the value for $G(\text{total})$ obtained from the test with the smaller aliquot of the concrete. The porosity of the concrete can then be calculated knowing the volume of the concrete. The equation for the volume of the gas is obtained by rearrangement of the equation for $G(\text{total})$.

* Parr Instrument Co., Moline, Illinois.

** Bell & Howell, CEC Division, Pasadena, California.

container very small (0.0045 L) and by using the high pressure container described earlier. The three possible hazards associated with this test are:

- Production of H₂ within a glove box
- Presence of a gas at high pressures (maximum to be tested 500 psi) within a glove box
- Presence of an explosive mixture of H₂ and O₂ in the glove box.

The production of H₂ and possible formation of a flammable mixture within the box itself is not a significant hazard because of the low production rate of H₂. Air flow through the box would have to be stopped for more than three years for the H₂ concentration in the glove box to reach its lower flammability limit in air (4 percent).⁹ The hazard associated with presence of a gas at a high pressure is not significant because of the small free volume in the high pressure container. If for some reason the gas vents while at 500 psi, the pressure within the glove box would still be less than atmospheric. The possibility of an explosion is minimized because the gas will always be at room temperature unless an external fire occurs. At room temperature, mixtures of H₂ and O₂ will not explode unless a source of ignition is present or if the pressure exceeds 1000 psi. The value for this pressure is based on an extrapolation of the spontaneous explosion limit for H₂-O₂ mixtures.¹⁰ In the present test, no source of ignition is present, and the possibility of an external fire has been minimized by removal of all flammable material from the glove box. If an explosion did occur, the only damage would be to the 3000 psi rupture disc. It would fail, and the gas would vent to the box. Again, because of the small amount of gas present (0.0045 L), this venting would not pressurize the box. Finally a shield is present to prevent the fragments of the rupture disc from damaging the glove box if the rupture disc fails.

Long-Term Low Dose Rate Test

As indicated earlier, the alpha dose rate in actual waste will be less than that used in the laboratory tests. For example, actual waste will probably have a dose rate $<4 \times 10^{14}$ eV/min per gram of concrete, while the laboratory tests have used higher dose rates. Tests had been performed earlier at two different dose rates (10^{16} and 10^{17} eV/min per gram of concrete) for portland Type I and high alumina concrete.³ No dose rate effect on the values of G(H₂) was observed. As a further test of dose rate effects, a test on each concrete was performed at a lower dose rate (about 4×10^{15} eV/min per gram of concrete) for the two types of cement.

Pu-238 added to the concrete. Also, these concretes were prepared in removable plastic molds. After the concrete had cured for several days, the molds were removed, and the samples were placed in steel test tubes that were then attached to the pressure transducers.

Pressure changes for the two samples are shown in Figure 4. The large scatter of the data is a result of temperature fluctuations since no attempt was made to control the temperature. Analysis of the gas after the tests showed that in both cases, the partial pressure of N_2 was unaffected by the radiolysis while that for O_2 decreased. This decrease resulted in the G values presented in Table 4. With high alumina cement, the O_2 pressure decreased faster than H_2 was produced, thus causing a decrease in the total pressure. The larger decrease in O_2 with high alumina cement compared to portland Type I cement has been observed with other samples. For both concretes, the pressure decrease was significant during the first 100 hours of the tests. After this, the pressure increased linearly for the portland Type I cement. The value for $G(\text{total})$, 0.23 molecules/100 eV is less than $G(H_2) + G(O_2)$, 0.43. This difference could be due to experimental error in calculating the change in O_2 pressure during the test from the difference between two relatively large numbers. $G(\text{total})$ for the high alumina concrete was not calculated because the pressure decrease was not linear.

PROGRAM

Funding for this program ends May 30, 1980. Four final experiments are in progress and will be completed by May 30, 1980.

- The high pressure experiment will be continued until the total pressure reaches 500 psig. At this time the gas will be analyzed for its composition and pressure effects.
- Compressive strengths of concretes dried at 200°C will be measured and compared with those of samples not dried. This will determine if drying decreases the effectiveness of concrete as a solidification matrix for incinerator ash.
- Water will be added to a concrete containing NO_2 to determine if NO_2 can significantly reduce $G(H_2)$ in presence of excess water as it does in concrete containing about 20 percent water.
- The rate of water absorption upon standing at ambient conditions by concrete dried at 200°C will be measured. This will give an estimate of how soon containers of concrete and actual waste have to be sealed after drying.

A final report summarizing all the results obtained in this program will be issued.

TABLE 1. Results of Irradiation of Two Aliquots of Portland Type I Concrete for High Pressure Test

Sample Number	Irrad. Time, hr	Final Pressure, psia	Composition, %			G Values			$G(O_2)/G(H_2)$
			H_2	O_2	N_2	$G(H_2)$	$G(O_2)$	$G(Total)$	
I-7	823	130 ^a	64.2	34.9	0.8	b	b	b	0.54
I-8	629	8.5	41.0	33.1	25.9	0.28	0.16	0.42	0.57

- a. Tests showed that this final pressure was low because a leak had developed.
- b. Not calculated because of the total void volume of the container was unknown, and a leak had developed.

TABLE 3. Composition of Concretes for Low Dose Rate Tests

Sample Number	Composition				Void Volume in Container, mL	Dose Rate, eV/(min) (g of concrete)
	Cement, g	Ash, g	Water, g ^a	Pu-238		
HAC-1	9.56	4.09	5.13	0.0064	23.5	4.1 x 10 ¹⁵
I-3	9.94	4.24	5.90	0.0073	20.2	4.4 x 10 ¹⁵

a. Added as about 0.2M H₂SO₄ to prevent precipitation of the plutonium. This is the amount of water that remained after curing.

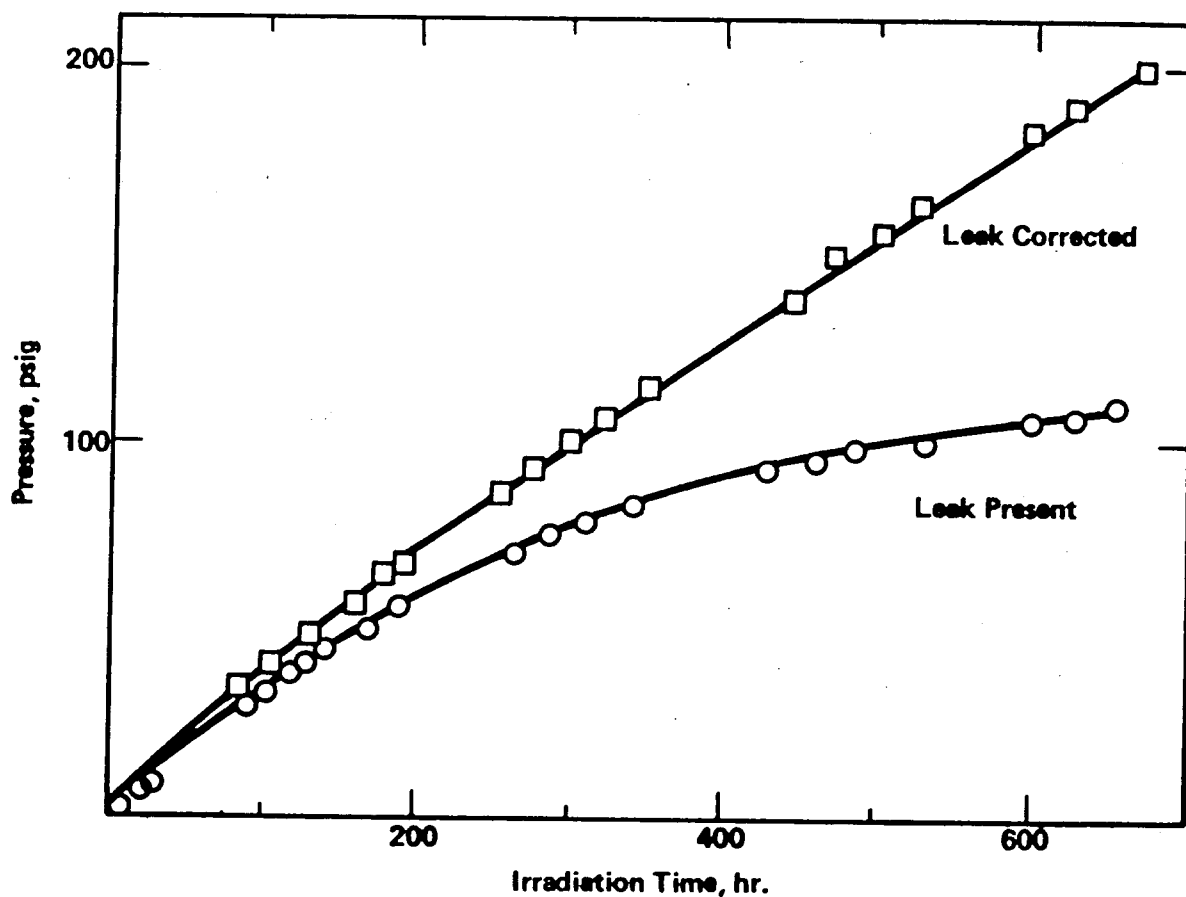


FIGURE 1. Radiolytic Pressure Increase with Portland Type I Concrete in the High Pressure Test

○ = Leak Present

□ = Current Test After Leak Corrected

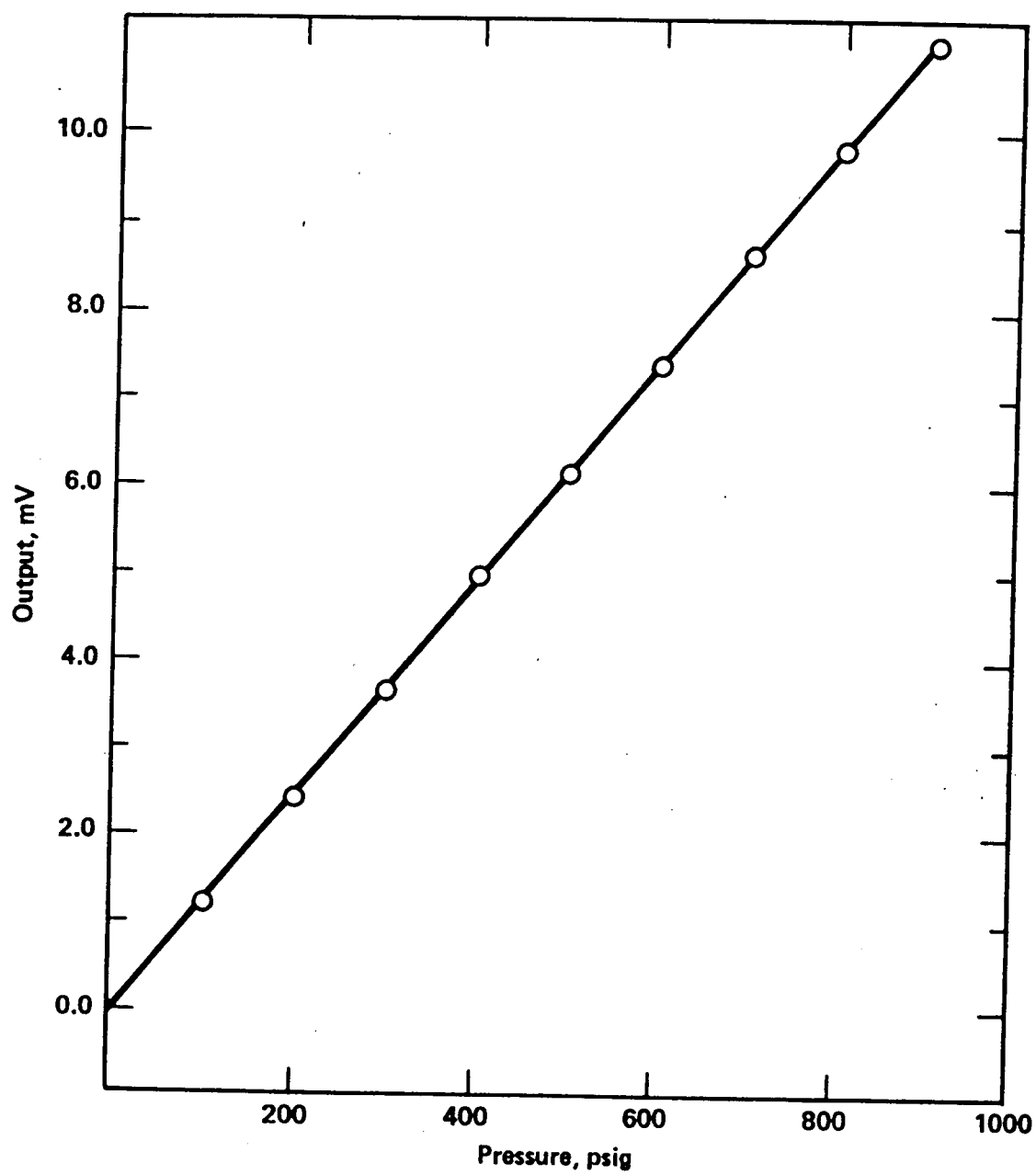


FIGURE 3. Calibration of the Pressure Transducer for the High-Pressure Test

Proceedings
of the
International Conference
on
DECOMMISSIONING AND DECONTAMINATION
and on
NUCLEAR AND HAZARDOUS WASTE MANAGEMENT

Volume 1

September 13-18, 1998
Denver, Colorado

Sponsored by

American Nuclear Society
U.S. Department of Energy
Colorado & Idaho Sections of the American Nuclear Society
Fuel Cycle & Waste Management Division
Environmental Sciences Division
Decommissioning, Decontamination and Reutilization Division



Published by the
American Nuclear Society, Inc.
La Grange Park, Illinois 60526 USA

GAS GENERATION IN MAGNESIUM-PHOSPHATE CEMENT SOLIDS INCORPORATING PLUTONIUM-CONTAINING ASH RESIDUE

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ABSTRACT

The applicability of acid-base cements, which have also come to be called chemically bonded ceramics (CBC), to Pu-containing residues within the DOE complex is being investigated. This preliminary inquiry considers CBC stabilization of ash residues from the inventory at the Rocky Flats Environmental Technology Site (RFETS). The ash residues have been successfully stabilized in CBC. Results of ongoing radiolytic gas generation measurements are discussed. Hydrogen release from CBC waste forms seems acceptable and lessons have been learned which will support successful production-scale application of acid-base cementation to the Rocky Flats ash residues.

INTRODUCTION

Approximately 125 t (metric tons) of Pu-containing residues exist within the U.S. Department of Energy (DOE) complex at former defense related facilities.¹ Among these holdings are over 20 t of ash, ash heel, soot and associated fines in storage at the former Rocky Flats Plant near Denver, Colorado. This material awaits stabilization into a form which is transportable to the Waste Isolation Pilot Plant (WIPP) in a TRUPACT-II shipping package, which accommodates maximum fissile loading through pipe component compatibility, which meets both the waste acceptance criteria and quality assurance mandates of the WIPP, and which satisfies safeguards termination goals by matrixing fissile material such that it is "practically irrecoverable" or, more generally, unattractive for diversion. Cold ceramification using CBC has proven effective for stabilizing fine debris tainted with Resource Conservation and Recovery Act (RCRA) regulated

hazardous metals into leach resistant ceramic-like monoliths through simple non-thermal preparation.²⁻⁴ CBC may be a favorable technology for stabilizing Pu-containing residues.

A primary component in acid-base cementation is the collection of amorphous silicates and aluminates commonly known and readily available as flyash. Since flyash is a base ingredient in the CBC process itself, cold ceramification of Pu-bearing ash residues, with the contaminated ash replacing some or all of the innocuous flyash in each batch, seemed a reasonable first step of inquiry for CBC application to the larger varying inventory of residues. Therefore, the applicability of CBC to the Rocky Flats ash inventory is being evaluated.

In application of acid-base cementation to this residue waste stream, the primary, and essentially sole, validated waste form performance criterion requiring testing at this time is characterization of radiolytic gas generation. As a new potential WIPP-bound waste form it is understood that gas generation characterization will be through the path of physical testing methodologies as opposed to through analytical techniques which have been developed to support TRUPACT-II loading of, principally, untreated wastes. This paper looks at the gas generation potential of monoliths formed with Rocky Flats ash and ash heel to bracket expected radiolytic gas generation rates among the population of CBC monoliths which will be created in large scale application of the process to Rocky Flats ash residues. In so doing, this data supports a go versus no-go decision regarding deployment of the process at Rocky Flats.

The gas generation standards facing TRUPACT-II-carried WIPP-bound wastes are based on prevention of explosive environments within either the free volume of a TRUPACT-II shipping package or any smaller confinement layer (e.g., the free volume of an individual container) during a presumed sixty day transport period.⁵ Accumulation of hydrogen is limited to five volume (generally interpreted as the more restrictive free volume) percent within any payload confinement layer over sixty days. Accumulation standards also exist for volatile organic compounds, but comparisons to this standard are not made in this paper as such species (the most notable and likely species being methane) have not yet accumulated significantly in any of the test systems in this project.

At the present time, a validated quantitative performance specification for satisfaction of the essentially qualitative safeguards termination unattractiveness goals has not yet been established, though suggested procedures have been developed.⁶ This paper does not, therefore, discuss actinide recoverability from CBC waste forms.

TECHNOLOGY BACKGROUND

Though largely overlooked in waste stabilization efforts to date, there exists a promising group of cementitious binding processes which are implemented with the operational simplicity of a nonthermal batch mix-and-set process, like typical hydraulic cements, but produce final solids with mechanical strength and component binding properties similar to those of thermally fused ceramics. The strength of these materials derives from their formation through acid-base reactions and the subsequent dominance of ionic and covalent bonding in the final structure. Such bonding is preferable to the weaker hydration and van der Waal's bonding which forms typical hydraulic concrete. The materials are rightly classified as acid-base cements but have also come to be called CBCs.⁷⁻⁸ The process itself has been referred to as cold ceramification in reference to the absence of heat requirements for curing, particularly relative to the high heat requirements associated with the production of materials typically called ceramic. A particularly well studied genre of CBC is the magnesium phosphate system which has been the subject of many patents, some fifty years old, and many practical commercial products.⁹⁻²⁶ The preponderance of phosphate based systems has given rise to another common name for these materials, that being chemically bonded phosphate ceramics.

Materials scientists A. S. Wagh and D. Singh* of Argonne National Laboratory recognized the potential of these materials for radioactive and mixed waste stabilization and have secured a patent, the exercise of which is freely available to any DOE facility, for such applications.²⁷ Their work has focused quite successfully on enhancement of the acid-base chemistry to favor metal, and particularly RCRA-regulated hazardous metal, fixation both as lesser soluble phosphates and then as bound phosphates within the final solid matrix.

Each of the particular formulations discussed in the listed references shares the commonality of solidification with tailored acid-base reactions, typically aided by the presence of flyash. Most of these reactions free magnesium from magnesia to join in any of a great variety of final phosphate compounds as determined by the particular species of phosphate introduction and other reacting components present. Various specific reacting systems differ with regards to rates and heats of reaction as well as with respect to final and byproducts produced. Some systems produce byproduct waste gases. The particular form of CBC being applied in this project is that which was successfully applied to mixed wastes at Argonne National Laboratory - West (ANL-W) as discussed in reference 4. It combines reacting binders of magnesia (reduced in reactivity through calcination or dead-burning) and monobasic potassium phosphate in the presence of water to form the primary system binder of hydrated magnesium potassium phosphate by the following reaction:



This system does not produce byproduct reaction gases during formation. The typical preferred batch composition is, by mass, one half ash, one third reacting binders, and one sixth added water. As will be noted later, water was actually introduced in excess of process requirements in this project to permit study of bound versus unbound water radiolysis response. Preferred binder introduction is as fine powders. Reaction kinetics and degree of completion are limited by diffusion at the magnesia surface. Mass distribution of reacting binders, as dictated by the stated reaction stoichiometry, is three parts calcined magnesia to approximately ten and one half parts monobasic potassium phosphate.

* A. S. Wagh and D. Singh may be reached at Energy Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne IL, 60439.

WORK DESCRIPTION

Ash residue samples from Rocky Flats have been obtained and stabilized in CBC at ANL-W. In this initial test, ten ash-containing CBC monoliths were produced. These monoliths are now serving as test specimens in waste form characterization activities.

Samples of pulverized incinerator ash, Item Description Code (IDC)^b 420, and ash heel (IDC 421) were obtained for this investigation. These are just two of several residue classifications associated with operations of the Rocky Flats incinerator but, together, these two IDCs comprise 96% of the approximately 20 t of incinerator-produced residue holdings at RFETS. The IDC 420 ash is the bottoms ash from a grate style, typically inefficient, incinerator which was subsequently pulverized in a ball mill. IDC 421 ash heel is the residue remaining after one or more attempts at actinide recovery from IDC 420 ash; fissile material remaining in ash heel is that which could not be economically recovered from the pulverized ash by conventional means. Typical incinerator feed included paper towels, wood filter frames, polyethylene bags, polyvinyl chloride bags, cotton coveralls and various rubber items.²⁸

The pulverized ash used in this study contained 0.3 wt% Pu of weapons grade distribution with 0.22 wt% of the actinides present being Am-241.²⁹ This ash had a density of ≈ 1 g/ml. A 2-step Loss on Drying (LOD) followed by a Loss on Ignition (LOI) test has been performed on the IDC 420 ash (RF Identification No. 07373028) used in the process demonstration. The LOD test held the sample at 100 °C for one hour. Pre and post LOD mass measurements indicate a 1 % mass loss in the LOD which is presumed to be due to unbound moisture removal. The subsequent higher temperature LOI heat up/cool down cycle occurred over eight hours and included two hours residence at the peak temperature of 1000 °C. Pre and post LOI mass measurements indicated a 9.8 % mass loss in the LOI which was attributed to ignition of residual organic matter. This finding of approximately 10% residual unoxidized organic material is in excellent agreement with findings in similar LOI tests done at RFETS.³⁰

The ash heel used in this study was of similar density and contained approximately 12 wt% actinides

of the same isotopic distribution as the ash.³¹ The ash heel did not have Rocky Flats identification labels. The heel came to be in ANL-W's possession following a repackaging operation and inventory reduction campaign at Lawrence Livermore National Laboratory in 1992. This heel was to have been used to support an actinide recoverability testing program several years ago. The program was canceled after ANL-W received the ash heel but before recoverability work could be initiated.³² Due to the highly oxidative nature of the actinide recovery attempts, this heel, like the inventory of IDC 421 ash heel at RFETS, is believed to be void of even trace reduced organic material. A verification LOI was not conducted.

These two samples, ash and ash heel, were conveniently placed at extremely low and fairly high ($\approx 92^{\text{nd}}$ percentile) actinide concentrations with respect to the concentrations present in the overall ash residue inventory at Rocky Flats (Figure 1) such that aliquoting and mixing of these two residue samples was a viable method to create a variety of samples of varying intermediate actinide concentrations and with varying residual organic presence. Consequently, a range of monoliths were able to be formed which represent the much larger inventory of monoliths which might be produced at RFETS.

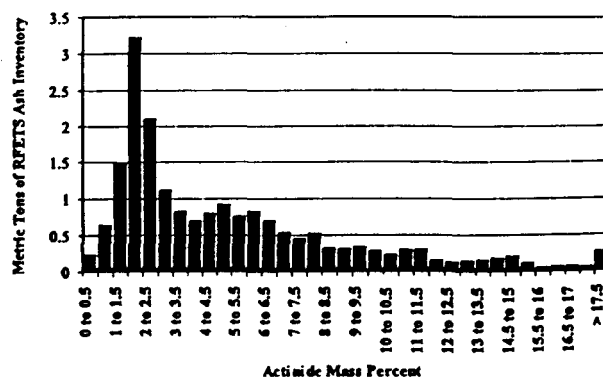


Figure 1: Mass Distribution of RFETS Ash Residues per Actinide Concentration.

Particle size distribution was not characterized with either the ash or heel. However, based on macroscopic inspection, it may be approximated that the ash varied from fine powder (50 μm) or less up to inclusion of small pieces with diameters of several millimeters. The ash heel was all fine powder. Neither elemental assays nor X-ray diffraction spectrums were obtained for either the ash or ash heel; deterministic characterization to great detail, as is typical for surrogate work, was not considered necessary as this study did, in fact, have

^b The Item Description Code label references a unique material identification system employed within the DOE complex.

actual RFETS ash inventory samples.

The primary focus of this study is characterization of radiolytic gas generation in actinide bearing CBC monoliths with an aim of bracketing the range of gaseous release rates, particularly of gaseous hydrogen but also of volatile organic species, which may be anticipated in application of CBC to the entire inventory of RFETS ash residues. To this end, the sample ash and heel was principally apportioned to support production of a set of seven 400-g monoliths for gas generation testing. Every effort was made to choose monolith production data points such that the largest possible coverage of the population of production possibilities at RFETS would be spanned. In so doing, fissile material loading was caused to range from 1 wt% to 5 wt% (referenced to final monolith mass) across the group of seven test monoliths, water was added in excess of actual requirements ranging from 1 wt% to approximately 6 wt%, and residual organic concentration varied from 0 wt% to 4 wt%.

It is believed that some ash in storage at RFETS may contain particularly high organic concentrations up to about 40 wt%,³³ i.e., these residues are almost as much ball-milled uncombusted feed as actual ash. However, as an actual stabilization campaign at RFETS will necessarily include feed prehandling, segregation, and mixing to satisfy fissile material loading constraints, opportunity will also be provided to consider and influence residual organic content in batch preparation. This opportunity, properly exercised, in combination with anticipated effective dilutions with innocuous flyash, is anticipated to keep residual organic concentrations in final monoliths in the low few percent range. That being the case, residual organic presence of the population of likely producible CBC monoliths at RFETS is well spanned by this test array. Together, then, the test array discussed herein is estimated to span a large fraction of the probable production population which may result from a CBC stabilization campaign at RFETS with regards to fissile loading, excess water presence and residual organic presence.

Details of ingredient additions for the seven monolith test array may be found in Table 1. The fabricated monoliths included necessary process binders (i.e., calcined magnesite (MgO) and monobasic potassium phosphate (KH_2PO_4)),^c water, and, for some

^c Both binders were provided by A. S. Wagh and D. Singh. The magnesite was originally analytical grade purchased from Mallinckrodt as the dead-burnt oxide and further calcined to reduce its

specimens, a low-Fe Class F Flyash^d as needed to complete the 50 mass percent ash contribution integral to the process. Also, this group of monoliths was purposefully formed with excess water to aid characterization of the water radiolysis effect.

Additionally, two 400-g monoliths were fabricated for actinide recoverability testing should a performance specification for actinide recovery from stabilized residues become validated. Finally, one 2-l monolith was formed for demonstration of the process at a likely scale of application at RFETS.

These ten CBC monoliths were fabricated in an air atmosphere plutonium handling glovebox in the Analytical Laboratory at ANL-W in November, 1997. Required fabrication equipment included a scale and a stand mixer.^e All mixing was done in high-density polyethylene containers. It is understood that radiation interaction with the plastic containers is itself a minor source of radiolytic gases. However, this source is extremely trace when compared to the gaseous emanation from within monoliths themselves and not significant. The seven 400-g monoliths being used for gas generation characterization were mixed in 250-ml polyethylene containers. Each monolith required a twenty minute mixing time and was sufficiently hardened within two hours to begin monolith post-mix handling.

The seven monoliths purposed for quantifying radiolytic hydrogen gas generation were carefully bagged out of the fabrication glovebox into filtered bags. Individual monoliths-in-filtered bags were then loaded into individual test canisters in a separate argon-atmosphere alpha glovebox dedicated to radiolytic gas quantification. Each test canister was aggressively purged with nitrogen for a minimum of twenty-four

reactivity. The monobasic potassium phosphate was food grade purchased from FMC.

^d Class F Flyash from the Jim Bridger Power Plant in Rock Springs, WY, was used. This ash was analyzed to be 65.4 wt%, 16.4 wt% and 5.03 wt% oxides of Si, Al, and Fe, respectively. It had a low lime content, less than 6wt%. It was quite fine, only 26% being retained on a 325 mesh (45 μm) sieve. It was supplied by Pozzolan International, P.O. Box 21679, Salt Lake City, UT 84121.

^e Arrow-850 mixer, available from Arrow Engineering, 260 Pennsylvania Ave, Hillside, NJ 07205, mounted on a custom mixer stand. The mixer shaft had a variable revolution per minute (rpm) capability with a referenced maximum speed of 1000 rpm and a maximum torque delivery of 0.8 N-m.

Table 1: Constituent Additions to Seven Monoliths Used in Gas Generation Characterization.

Monolith No.	IDC 420 Ash (g)	IDC 421 Ash Heel (g)	Class F Flyash (g)	MgO (g)	KH ₂ PO ₄ (g)	Water (g)	Total Mass (g)
1	161.7	30.6	0.00	29.3	99.1	95.7	416
2	86.1	24.3	77.0	29.3	99.4	90.4	407
3	90.8	96.4	0.00	29.7	98.7	86.8	402
4	0.00	33.4	153.8	29.3	98.9	83.5	399
5	0.00	101.1	87.2	29.4	99.4	78.7	396
6	0.00	166.4	21.0	29.6	99.2	89.5	406
7	0.00	32.7	153.6	30.1	99.2	69.8	385

hours then sealed. The moment of canister sealing (Table 2) denotes the beginning of the radiolytic gas accumulation test period for each sample. All canisters were sealed with initial nitrogen-atmosphere pressures of approximately 0.23 MPa. This value was chosen to provide sufficient driving pressure for up to ten sampling events for each canister over the duration of the experiment while, simultaneously, keeping total head space density, and, therefore, dilution of radiolytic gas by inert carrier gas, to a minimum. The free volume of the test canister serves as the gas accumulation region.

Use of the filtered bags, custom fabricated at ANL-W for this purpose, allowed caps to be removed from monolith containers within the breathable bags thereby allowing gas diffusion from the polyethylene containers containing individual monoliths into the larger head spaces of the respective gas generation test canisters while still maintaining a high level of particulate containment to protect the new test canisters from surface alpha contamination. Parameters germane to analysis of radiolytic gas data for the seven test monoliths are detailed in Table 2. Canister head space sampling began with a first round of sampling in January, 1998. A second round of head space samples

was extracted and analyzed in April, 1998. The canisters remain sealed and are still actively accumulating radiolytically generated gases as of this writing.

DATA

Stabilization of Rocky Flats ash residues into high integrity solids using CBC has been demonstrated. Fabrication proceeded normally. All batches were readily mixed and desired binding reactions proceeded at normal rates. Single use peak temperature recorders were used to track peak curing temperatures. The average peak curing temperature for all monoliths was about 323 K. All solid monoliths, based on rough comparison of mass to volume, have densities of about 1.9 g/ml, which is typical for the process.

The most recent round of generated gas characterization data is listed in Table 3. Thus far, the only regulated gas to have accumulated in any of the test canisters at significant levels is diatomic hydrogen. Therefore, only characterization of radiolytic hydrogen generation is considered here.

Table 2: Parameters Essential to Radiolysis Gas Data Analysis.

Monolith No.	Date and Time of Test Canister Isolation	Energy Deposition Rate (eV/day)	Organic (mass percent)	Added Water (mass percent)
1	12/04/97 08:45	5.92E+21	3.81	23.0
2	12/23/97 13:30	4.48E+21	2.08	22.2
3	12/15/97 14:15	1.65E+22	2.21	21.6
4	12/16/97 14:30	5.56E+21	0	20.9
5	12/10/97 14:00	1.68E+22	0	19.9
6	12/11/97 14:45	2.77E+22	0	22.1
7	12/09/97 14:30	5.44E+21	0	18.1

Table 3: Mid-April 1998 Gas Canister Sampling Data.

Monolith No.	Date and Time of Head Space Sampling	Accumulation Period (days)	Canister Pressure (Pa)	Canister Temperature (K)	Diatomic Hydrogen Presence (ppm)
1	04/14/98 09:15	131.02	2.363E+5	296.1	6,028
2	04/13/98 13:30	111.00	2.305E+5	295.3	2,996
3	04/13/98 10:45	118.85	2.322E+5	295.7	10,993
4	04/13/98 11:45	117.89	2.287E+5	295.5	2,837
5	04/10/98 13:30	120.98	2.322E+5	295.7	7,086
6	04/10/98 15:00	120.01	2.347E+5	295.6	14,310
7	04/10/98 11:45	121.89	2.301E+5	295.9	1,042

Each sampling event involves expansion of an isolated canister environment into a previously evacuated sample line followed by canister re-isolation followed by expansion of the gaseous sample aliquot in the sample line through a gas chromatography system.^f At the point the sample line and test canister are connected, system temperature (to three significant digits) and pressure (within 100 Pa) are recorded.^g The free space volume of each canister and sample line system has been determined to be 6.750 liters (within 0.035 liters). Simultaneous knowledge of system temperature, pressure and volume allows calculation of total moles of gas in the system by ideal gas relations (entirely reasonable application at low pressure). The product of total moles present and concentration of any species (from gas chromatography) yields an accurate measure of the moles of any particular species present in the system at time of sampling. For the first sampling event in January, 1998, moles of hydrogen, for instance, found in the system (i.e., any single CBC monolith in test canister system) were attributed to production by radiolysis between the time of canister sealing and head space sampling.^h All sampling events after the first include consideration of gas species taken from the system in previous sampling events in summing to

determine total numbers of a particular gas species produced.

The most recent data-gathering also found indication of methane presence (at about the detection limit of the gas chromatography system) in the head space of the monolith among the test array having the highest organic loading. Methane is certainly one of the most common radiolytically produced gases from organic sources and worthy of discussion as volatile organic vapors/gases are also regulated by TRUPAC-II loading guidance. However, due to its occurrence at a very low concentration in only a single sample, correspondingly imprecise prediction statistics does not support meaningful discussion of methane production rates from organic containing CBC monoliths at this time.

Bracketing of radiolytic gas generation and release rates will be through calculation of "G-values" which include normalization with respect to ionizing energy deposition. As energy deposition is itself a function of fissile loading, the G-value normalization leaves only the two parameters of water concentration and residual organic material concentration against which calculated G-values may be compared. The units of G-value are, broadly, gas produced per ionizing energy deposited, and, more specifically regarding diatomic hydrogen, molecules of the hydrogen produced per one hundred electron volts (eV) deposited. Each of the seven hydrogen G-values computed for each of the seven test monoliths is the quotient of molecules of hydrogen to have been produced in the system during the period of accumulation (i.e., sum of molecules of hydrogen present in the system at the time of sampling and molecules of hydrogen taken from the system in previous sampling events) to the total ionizing energy which had been deposited in the system during the

^f Hewlett Packard 5890 Series II Gas Chromatograph.

^g Pressure measurement is with an in-line Mensor 2100 DPG fabricated by Mensor Corporation, 2230 IH 35 South, San Marcos, TX 78666.

^h Note: earlier work with nonradioactive CBC samples investigated gaseous diffusion rates through the material and concluded that such diffusion was sufficiently rapid to negate consideration of production to release time lag effects from this analysis methodology.

period since test canister sealing (various dates in December, 1997, as listed in Table 2) and the time of sampling (April, 1998, specific dates listed in Table 3).

The seven computed G-values for the test array, based on approximately four months of radiolytic gas accumulation, are listed in Table 4 and plotted against added water content and against organic content in Figure 2.

Table 4: Hydrogen G-Values Based On Mid-April 1998 Test Canister Sampling.

Monolith No.	Hydrogen G-Value (molecules of H_2 /100 eV deposited ionizing energy)
1	0.303
2	0.230
3	0.215
4	0.164
5	0.134
6	0.167
7	0.0597

Scanning from left to right in Figure 2, the order of data points correspond to monoliths 7, 5, 4, 6, 2, 3, and 1. It should be noted that the "wt% water" axis in Figure 2 refers only to added water and its relative fraction of the total final monolith mass (as detailed in Table 1) and does not attempt to account for water produced in the desired acid-base binding reaction(s).

As stated previously, this data gathering is intended only to bracket gas generation potentials and does not suppose to develop a conclusive predictive model of radiolysis in CBC waste forms. Nonetheless, a simple regression fit to the data, first order with respect to added water weight percent and first order with respect to residual organic weight percent, has been performed ($r^2 = 0.98$). The perimeter of the plane formed by this fit is included in Figure 2. The statistics of this fit estimate the G-value for hydrogen to increase by 0.024 for each weight percent of added water (relative to final mass) in excess of stoichiometric requirements and, similarly, the regression fit estimates the G-value for hydrogen to increase by 0.028 for each weight percent of residual organic material present in the final waste form. For both excess water and residual organic matter, the G-value response seems quite linear. A most important observation to be gleaned from the plot of Figure 4 is that hydrogen G-value response for water is essentially zero at about 16 wt% added water and less. This

demarcation corresponds to the amount of water believed to be structurally fixed in the hydrated magnesium potassium phosphate which binds these monoliths. This demonstrates that bound water is essentially unavailable for degradation by radiolysis into gaseous species and that only unbound water in the pore space of final waste forms is available to contribute to hydrogen generation by radiolysis. This effect is not unique to the CBC waste forms as it has also been noted in more conventional hydration-bonded based solidification processes.³⁴

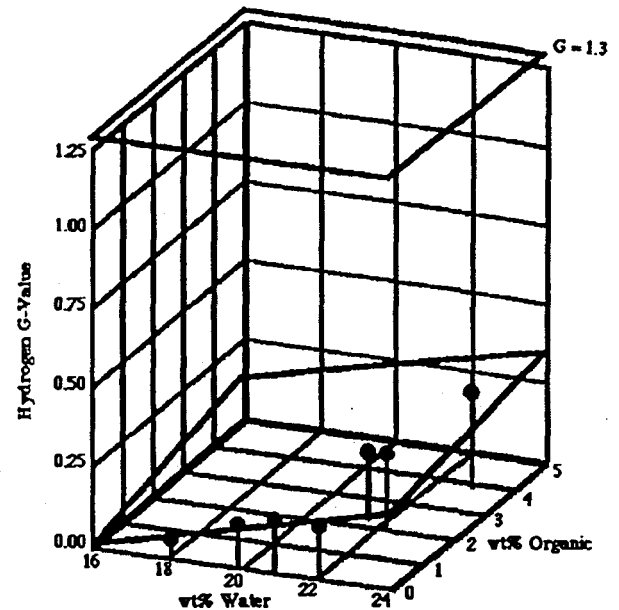


Figure 2: Plot of Calculated Diatomic Hydrogen "G-Values" (i.e., Molecules of H_2 Being Created and Released per 100 eV of Ionizing Energy Deposited) Versus the Two Principal Hydrogen Sources, Added Water and Added Residual Organic Matter (From IDC 420 Ash). Includes Planar Fit to Data ($R^2 = 0.98$) and Calculated Target Performance Plane at $G = 1.3$.

Figure 2 also includes, at the top of the plot, a perimeter defining a plane at the G-value equals 1.3 level. This plane represents an approximate performance specification against which the actual G-value data may be considered. This performance specification estimate was back-calculated as the hydrogen gas generation response of a final waste form, regardless of type, that would produce a 5 % hydrogen concentration within the out-of-drum free space volume of a TRUPACT-II shipping package (approximately three cubic meters) during a sixty day accumulation period (per TRUPACT-II requirements) with a source term of fourteen pipe component-in-drum waste

packages each of which contains 167 grams of Pu-239 and associated other actinides in a typical weapons grade distribution. This calculation attributed a collective $2E+26$ eV of ionizing energy to be deposited in the described system with relative nuclide-specific contributions to net ionizing energy deposition for the composition as follows: Pu-238, 2.2 %; Pu-239, 70.1 %; Pu-240, 16.1 %; Pu-241, trace; Pu-242, trace; and Am-241, 11.6%.

CONCLUSIONS AND DISCUSSION

Monolith fabrication with Pu-containing ash residues proceeded without abnormal occurrences. Neither the IDC 420 ash nor the IDC 421 ash heel stabilized in this study resisted stabilization by the acid-base cementation process discussed herein. Mixing properties, reaction rates and setting times with the Pu-bearing materials in an air-atmosphere glovebox were no different than without Pu and outside a controlled atmosphere. There is no known reason to consider some portions of the ash inventory at RFETS to have constituent properties significantly different from the ash and ash heel stabilized in this project. It is, therefore, concluded that CBC is a viable technology for RFETS ash residue stabilization.

As the fabricated test array included a wide range of residue waste loadings ranging from less than ten to almost fifty percent, (refer to Table 1), it may be concluded that the process is versatile and will easily accommodate various waste feed concentrations in a stabilization campaign which also meets strict pipe component fissile loading requirements.

Radiolytic hydrogen generation within CBC monoliths seems to be within acceptable limits. Or, more precisely, insight has been gained to direct CBC production to ensure that radiolytic hydrogen generation will be within acceptable limits. The data presented here provides two clear directives for operational planning in acid-base cementation of RFETS ash residues. These are 1) water addition should be at levels to support reaction stoichiometry (about 16 wt% of constituent additions) while avoiding excess and 2) blending/batching should be employed to keep organic concentrations low.

ACKNOWLEDGMENTS

The project was funded by the DOE's Plutonium Focus Area under contract W-31-109-ENG-38. The author wishes to thank A. S. Wagh and D. Singh for

calling our attention to the fifty year old technology of acid-base cementation as a viable and now seemingly obvious option for waste stabilization and Y. Macheret of the DOE's Idaho Operations Office for both seeing the connection between ash-based cold ceramification and the Rocky Flats ash residues and for recognizing ANL-W's Pu handling and chemistry facilities as an ideal location for this demonstration.

REFERENCES

1. *Ash Residues End State Trade Study, Volume 1*, U.S. Department of Energy Idaho Operations Office, Plutonium Focus Area, DOE/ID-10560 (1996).
2. A. S. Wagh, J. C. Cunnane, D. Singh, D. T. Reed, S. Armstrong, W. Subhan, and N. Chawla, "Chemically Bonded Phosphate Ceramics for Radioactive and Mixed Waste Solidification and Stabilization," *Proc. of the Waste Mgmt. '93 Conf.*, Tucson, AZ, (1993).
3. A. S. Wagh, D. Singh, S. Y. Jeong, and R. V. Strain, "Ceramicrete: Stabilization of Low-Level Mixed Wastes - A Complete Story," *Proc. 18th USDOE Low-Level Rad. Waste Mgmt. Conf.*, Salt Lake City, UT, May 20-22, 1997 (1997).
4. D. Singh, D. B. Barber, A. S. Wagh, R. V. Strain, and M. Tlustochowicz, "Stabilization and Disposal of Argonne-West Low-Level Mixed Wastes in Ceramicrete™ Waste Forms," *Proc. of the Waste Mgmt. '98 Conf.*, Tucson, AZ, March 1-5, 1998 (1998).
5. *TRUPACT-II Safety Analysis Report*, Section 1.2, Package Description, Revision 16 (1997).
6. Pu Recoverability Testing Version 3.3, supplied by Tim Burns of Los Alamos National Laboratory (1997).
7. D. M. Roy, "New Strong Cement Materials: Chemically Bonded Ceramics," *Science*, 235, p. 651-658 (1987).
8. D. D. Double, "Chemically Bonded Ceramics: Taking the Heat Out of Making Ceramics," *J. Mater. Educ.*, 12, p. 353-381 (1990).
9. E. Wainer and A. Salomon, "Quick Setting Cement," U.S. Patent No. 2,391,493 (1945).

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... made of ... for ...

10. H. H. Greger, "Phosphate Cements," U.S. Patent No. 2,450,952 (1948).
11. C. H. Schwartz, "Patching Method," U.S. Pat. No. 3,821,006 (1974).
12. R. W. Limes and R. O. Russell, "Process for Preparing Fast-Setting Aggregate Compositions and Products of Low Porosity Produced Therewith," U.S. Pat. No. 3,879,209 (1975).
13. R. F. Stierli, C. C. Tarver, and J. M. Gaidis, "Magnesium Phosphate Concrete Compositions," U.S. Pat. No. 3,960,580 (1976).
14. H. J. Horvitz and A. P. Gray, "Matrix Forming Compositions," U.S. Pat. No. 4,152,167 (1979).
15. E. A. Tomic, "High-Early-Strength Phosphate Grouting System for Use in Anchoring a Bolt in a Hole," U.S. Pat. No. 4,174,227 (1979).
16. E. A. Tomic, "Phosphate Cement and Mortar," U.S. Pat. No. 4,394,174 (1983).
17. T. Sugama and L. E. Kukacka, "Magnesium Monophosphate Cements Derived from Diammonium Polyphosphate Solutions," *Cem. and Concr. Res.*, 13, p. 407-416 (1983).
18. T. Sugama and L. E. Kukacka, "Characteristics of Magnesium Polyphosphate Cements Derived from Ammonium Polyphosphate Solutions," *Cem. and Concr. Res.*, 13, p. 499-506 (1983).
19. T. Sugama and L. E. Kukacka, "Magnesium Phosphate Glass Cements with Ceramic-Type Properties," U.S. Pat. No. 4,436,555 (1984).
20. F. G. Sherif and E. S. Michaels, "Fast-Setting Cement From Liquid Waste Phosphorus Pentoxide Containing Materials," U.S. Pat. No. 4,487,632 (1984).
21. F. G. Sherif and A. G. Ciamei, "Fast-Setting Cements from Superphosphoric Acid," U.S. Pat. No. 4,734,133 (1988).
22. E. A. Tomic, "Phosphate Cement Including Flyash for High-Strength Concrete-Like Products," U.S. Pat. No. 4,749,413 (1988).
23. B. E. I. Abdelrazig, J. H. Sharp, P. A. Siddy, and B. El Jazairi, "Chemical Reactions in Magnesia-Phosphate Cement," *Proc. Br. Ceram. Soc.*, 35, p. 141-154 (1984).
24. B. E. I. Abdelrazig, J. H. Sharp, and B. El-Jazairi, "The Chemical Composition of Mortars Made from Magnesia-Phosphate Cement," *Cem. and Concr. Res.*, 18, p. 415-425 (1988).
25. B. E. I. Abdelrazig, J. H. Sharp, and B. El-Jazairi, "The Microstructure and Mechanical Properties of Mortars Made from Magnesia-Phosphate Cement," *Cem. and Concr. Res.*, 19, p. 247-258 (1989).
26. A. K. Sarkar, "Phosphate Cement-Based Fast-Setting Binders," *Ceram. Bull.* 69(2), p. 234-238 (1990).
27. A. S. Wagh and D. Singh, "Method for Stabilizing Low-Level Mixed Wastes at Room Temperature," U.S. Pat. No. 5,645,518 (1997).
28. Facsimile from Gary Thompson (1997).
29. W. R. Mosby, "NDA Measurements Performed on Rocky Flats Ash," Intra-Laboratory Memo TD-NA-WRM-97-041 (1997).
30. Telephone conversation with Donald Thorp (1997).
31. W. R. Mosby, "NDA Measurements Performed on Rocky Flats Ash Heel," Intra-Laboratory Memo TD-NA-WRM-97-042 (1997).
32. B. Gail Walters, "Rocky Flats Ash Heel," Intra-Laboratory Memo (1997).
33. Conversation with Gary Thompson (1998).
34. E. W. McDaniel and D. B. Delzer, "FUETAP Concrete," Chapter 9 in *Radioactive Waste Forms for the Future*, Eds. W. Lutze and R. C. Ewing, Elsevier Science Publishing Company, Inc., p. 565-588 (1988).

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RADIOLYTIC GAS PRODUCTION FROM TRITIATED WASTE FORMS

GAMMA AND ALPHA RADIOLYSIS STUDIES

NED E. BIBLER

ERROL G. OREBAUGH

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PREPARED FOR THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION UNDER CONTRACT AT(07-2) 1

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Printed in the United States of America

Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

Price: Printed Copy \$4.00; Microfiche \$3.00

RADIOLYTIC GAS PRODUCTION FROM TRITIATED WASTE FORMS

GAMMA AND ALPHA RADIOLYSIS STUDIES

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PREPARED FOR THE U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION UNDER CONTRACT AT(07-2)-1

ABSTRACT

Radiolytic gas production during long-term storage of tritiated waste was estimated from gamma and alpha radiolysis tests to determine the extent of pressurization in sealed containers. Two forms of simulated wastes were irradiated with ^{60}Co gamma rays or ^{244}Cm alpha particles: concrete for solidification of tritiated water and vermiculite for solidification of tritiated octane or vacuum pump oil. Results of these test irradiations were used to estimate the effects of beta radiolysis. For concrete, the gamma and alpha radiolysis results predicted that H_2 will be formed by tritium beta particles with an initial rate of 0.1 to 0.3 molecule for every 100 eV of energy absorbed. Also, as the H_2 pressure increases, this 100-eV yield decreases because of a reaction removing H_2 . Eventually, a steady state pressure that depends on the radiation intensity will be attained. For intensities less than 10^5 rads/hr, the steady state pressure will be less than 20 psi. O_2 in the air sealed with the concrete will be almost completely depleted, and N_2 will be unaffected. For the organic materials sorbed onto vermiculite, the gamma and alpha radiolysis results predicted that H_2 and traces of CH_4 and CO_2 will be produced. For tritium beta particles, the 100-eV yields for H_2 based on energy sorbed by the organic materials are 4.4 for octane and 2.2 for vacuum pump oil. In the containers, steady state H_2 pressure will not be attained at pressures up to at least 200 psi. As with the concrete, O_2 will be nearly completely depleted and N_2 will be unaffected. The 100-eV yield for H_2 production was used to calculate pressure increases in conceptual tritiated waste packages.

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RADIOLYTIC GAS PRODUCTION FROM TRITIATED WASTE FORMS GAMMA AND ALPHA RADIOLYSIS STUDIES

INTRODUCTION

Various types of waste materials containing tritium, ^3H , from nuclear processing facilities are incorporated into solid materials and packaged for long-term storage and isolation from the environment. Current solidification methods are incorporation into cement-plaster mixtures for aqueous wastes and sorption onto vermiculite for organic wastes.¹ These materials are then sealed in steel drums for storage. Other solidification methods such as incorporation into stable organic polymeric materials are also being investigated.²

During long-term storage of the waste, ^3H beta radiolysis of the water or organic materials will produce H_2 gas. H_2 could eventually pressurize the containers or produce flammable gaseous mixtures. Although the radiolysis of water and of many organic compounds has been extensively studied in the pure state,^{3,4} materials have not been irradiated in matrices suitable for storage of radioactive waste. Even though certain predictions of radiolytic gas behavior can be made from results of radiolysis of the pure compounds, the pressurization or flammability hazards during long-term storage can best be evaluated from radiolysis of the waste form itself.

This report presents an estimation of H_2 production from *in situ* beta radiolysis of a concrete containing tritiated water and of vermiculite containing sorbed tritiated organic waste. Estimates were based on experimental data for the 100-eV yields of H_2 from ^{60}Co gamma and ^{244}Cm alpha radiolysis of the two waste forms. The estimated rate of H_2 for ^3H beta radiolysis was interpolated from the rates of gamma and alpha radiolysis as a function of linear energy transfer (LET) of the three radiations. LET, the average amount of energy lost per unit path length as the radiation passes through a substance, strongly affects the efficiency of radiolytic decomposition and, consequently, gas production.⁵ The LET values for ^{60}Co gamma and ^{244}Cm alpha radiolysis bracket that of ^3H beta radiolysis.⁵ Once the 100-eV yield for H_2 production for ^3H beta radiolysis was estimated, this value was used to calculate pressure increases in containers of tritiated waste.

This approach was chosen rather than using ^3H as the radiation source because this laboratory is especially suited for gamma and alpha radiolysis studies. For gamma radiolysis, many experiments could be performed over a wide dose and dose rate range with any of four ^{60}Co sources. For alpha radiolysis, sufficient ^{244}Cm was available along with facilities for easily performing several such experiments.

Samples of concrete or vermiculite containing sorbed organic material were irradiated. These samples were sealed in steel containers that had attached pressure gauges and sampling valves. During radiolysis, the pressure was monitored; after radiolysis, the gas was sampled and its composition was determined by gas chromatography.

GAMMA AND ALPHA RADIOLYSIS OF CONCRETE WASTE

A mixture of portland cement and gypsum-perlite plaster is currently used for solidification of tritiated aqueous waste.¹ The waste water is mixed with the dry cement-plaster powder in the ratio of nominally 1:1.7 by volume or 1:1.4 by weight with 0.8 g/mL as the bulk density of the dry material. For the gamma radiolysis tests, the concrete was cast in a glass container with an attached pressure gauge and sampling valve. The pressure gauge and sampling valve were separated from the irradiation container by several feet of 1/8-inch-ID steel tubing. The alpha radiolysis tests were performed in glove boxes. The ^{244}Cm was dissolved in the water used to make the concrete, thus ensuring that ^{244}Cm was in direct contact with the compounds of the concrete. Each concrete sample was cast in a steel tube that was then sealed to a pressure gauge and sampling valve.

Gamma Radiolysis Tests

The gamma radiolysis tests determined the effects of dose rate and total dose on the rate of H_2 production. Results of these tests indicated that the initial rate of H_2 production was proportional to dose rate. However, in terms of molecules produced per 100 eV of energy absorbed (G value), the rate was independent of dose rate and was 0.03 molecule/100 eV from 8.9×10^4 to 2.6×10^7 rads/hr. As the radiation dose increased and consequently the H_2 pressure increased, the H_2 pressurization rate decreased until eventually a steady state pressure was attained. This indicates the occurrence of a radiolytic back reaction removing H_2 . The magnitude of this steady state pressure decreased with the dose rate. This behavior has also been observed in gamma radiolysis of another type of concrete containing simulated fission product wastes.⁶ In these gamma radiolysis tests, O_2 in the air sealed in the container was partially consumed and N_2 was unaffected.

Results and Discussion

Radiolytic pressure increases for two samples of concrete irradiated in containers of nearly equal free volumes are shown in Figure 1. The attainment of steady state pressures that are dependent on dose rate is clearly indicated. Gas composition at the end of the tests was 70% H₂, 27% N₂, and 3% O₂. Comparison of the individual partial pressures before and after radiolysis confirmed that H₂ was the only gas produced. Also, N₂ was unaffected by the radiolysis, and O₂ was ~75% consumed. O₂ consumption has also been observed in radiolysis of the concrete containing simulated fission product waste.⁶ Data in Figure 1 also indicate that the initial H₂ production rate is higher at the higher radiation intensity. However, when based on the amount of energy absorbed, the production rates were equal.

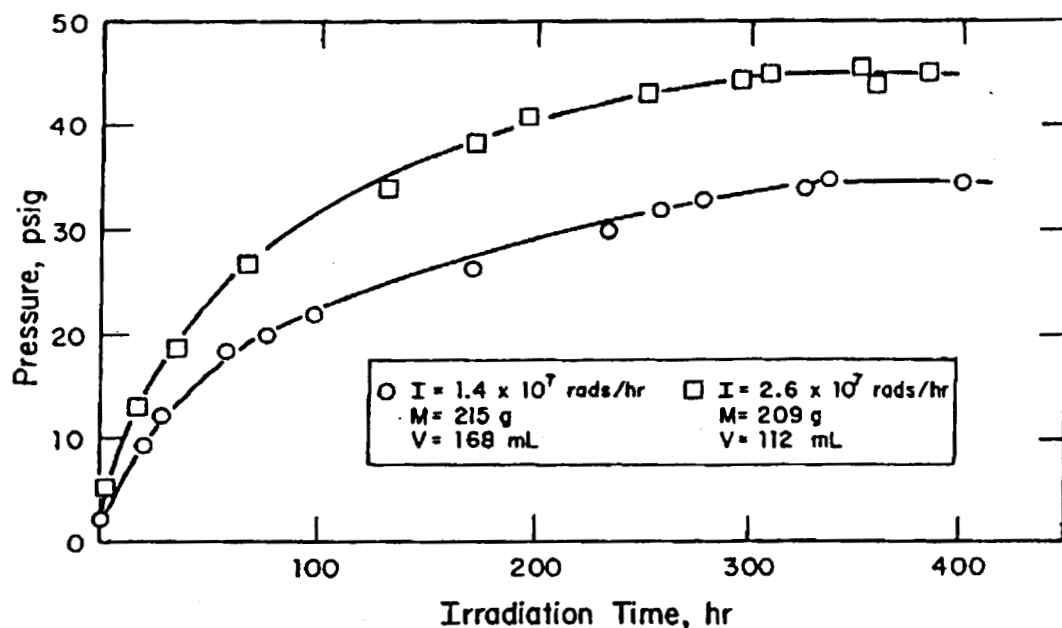


FIGURE 1. Pressurization from Gamma Radiolysis of Concrete at 47°C

G(H₂) was calculated from

(1)

$$G(H_2) = \frac{S \cdot V \cdot N \cdot 100}{R \cdot T \cdot M \cdot I \cdot C}$$

where

S = initial slope, psi/hr

V = gas volume, liter

N = Avogadro's number, molecules/mole

R = gas constant, psi (liter/mole)(°K)

T = temperature, °K

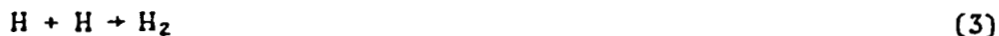
M = mass of cement irradiated, g

I = dose rate, rads/hr

C = conversion factor, 6.24×10^{13} eV(g)(rad)

For both samples, G(H₂) was 0.03 ± 0.01 molecule/100 eV.

To determine the radiation intensity dependence of the steady state pressure over a wider dose rate range, samples were irradiated at two lower dose rates (3.9×10^5 and 8.9×10^4 rads/hr). At these dose rates, irradiating the samples was impractical. Thus, the sample containers were back-pressurized with H₂ until radiolytic H₂ pressurization ceased. Results for all four dose rates are shown in Figure 2; the error bars indicate the reproducibility of the tests. This attainment of a steady state pressure and its dose rate dependence are consistent with the free radical model for H₂ production from gamma radiolysis of water.³ The oxide components of the cement and plaster are not drastically altering the radiation chemistry of the water. In the free radical model, H₂ is formed by recombination of H atoms produced by the radiation and destroyed by OH radicals, the other major species produced by radiolysis of water. Pertinent reactions are



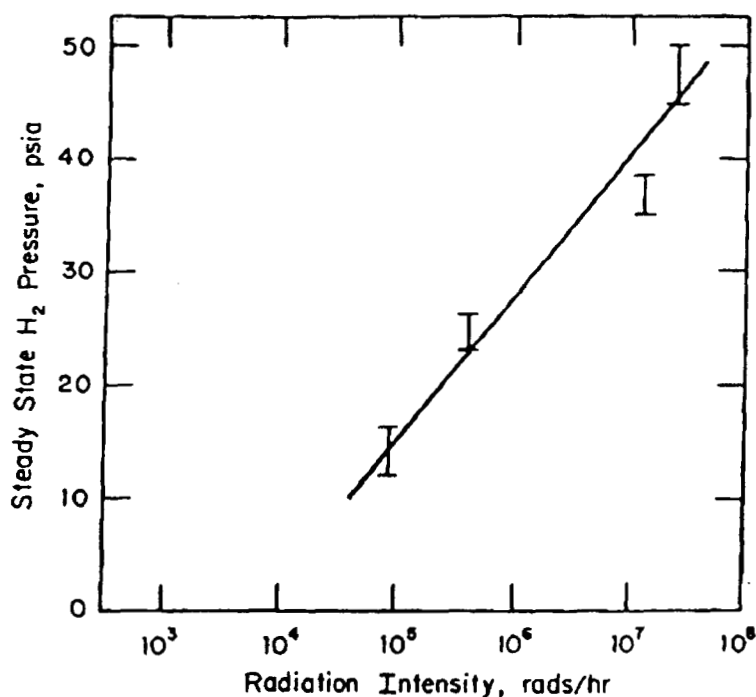


FIGURE 2. Effect of Dose Rate on Steady State H₂ Pressure from Gamma Radiolysis of Concrete

When the rates of Reactions 3 and 4 become equal, a steady state H₂ pressure is attained. Higher dose rates increase the rates of both 3 and 4 but increase 3 faster because 3 involves two radicals.⁷ Thus, at higher dose rates, higher H₂ pressures are necessary to compensate for the larger increase in the rate of 3.

Tests at 8.9×10^4 and 3.9×10^5 rads/hr agreed with those obtained at the higher dose rates. $G(\text{H}_2)$ was 0.03, O₂ was partially consumed, and N₂ was unaffected. The steady state H₂ pressure was independent of the gas volume. This pressure was also observed in gamma radiolysis of concrete containing simulated fission product waste.⁶ Identical pressurization rates were obtained at the same dose rate whether the concrete sample was cured 1 or 20 days. Results were also identical within water: cement-plaster volume ratios of 1:1.7 to 1:4.3 (1:1.3 to 1:3.4 by weight) with 0.8 g/mL as the bulk density of the dry material.

A final gamma radiolysis test determined the extent of O₂ depletion from the air sealed with the concrete. In previous tests, the entire gas was removed from the sealed system for analysis because earlier results had shown that incomplete mixing occurred during radiolysis due to the small tubing connecting the irradiation container to the pressure gauge and sampling valve. In absence of these latter components, 95% of the O₂ was consumed rather than ~75% as found earlier. Another

and sampling valves. The range of the alpha particles in the concrete is ~0.01 mm; thus, all the alpha energy was absorbed by the sample. For four tests with 11.5 g of concrete and 0.84 to 32 mg of ^{244}Cm , $G(\text{H}_2)$ was independent of the amount of ^{244}Cm and was 0.6 molecule/100 eV. This value is 20 times larger than that obtained for gamma radiolysis. This increase is not unexpected because $G(\text{H}_2)$ from liquid water is ~4 times larger for alpha than for gamma radiation.³ As with gamma radiolysis, O_2 was partially consumed and N_2 was unaffected. In contrast to gamma radiolysis, a steady state pressure was not attained even at ~200 psi H_2 . Failure to attain a steady state pressure was also observed in another study concerning alpha radiolysis of concrete containing simulated fission product waste.⁶

Results and Discussion

Figure 3 shows the radiolytic pressure increase for a sample of concrete containing 0.84 mg of ^{244}Cm . At the end of this test, the gas composition was 54% N_2 , 40% H_2 , and 6% O_2 . Comparison of partial pressure of N_2 and O_2 before and after radiolysis indicated that N_2 was unaffected and O_2 was ~60% consumed. $G(\text{H}_2)$ was calculated from

$$G(\text{H}_2) = \frac{S \cdot V \cdot N \cdot 100}{R \cdot T \cdot I} \quad (7)$$

where all the quantities except the dose rate I are identical to those defined on page 8 for the gamma radiolysis tests. I was calculated from the amount of ^{244}Cm present, its specific activity (80.9 Ci/g),¹⁰ and the energy of its alpha particles (5.8 MeV).¹⁰ For four separate tests with 0.84, 6.6, 13, and 32 mg of ^{244}Cm , $G(\text{H}_2)$ was 0.63 ± 0.07 molecule/100 eV. The dose rate for these amounts of ^{244}Cm was 7.5×10^4 to 2.8×10^6 rads/hr, and indicated, in agreement with the gamma radiolysis results, that $G(\text{H}_2)$ was independent of dose rate.

Radiolytic pressurization in another alpha radiolysis test is shown in Figure 4. This test was made to demonstrate that steady state pressure was not attained even at 200 psi. Failure to attain a steady state pressure, as in gamma radiolysis, probably results from the different modes of energy transfer by the two radiations. Alpha particles because of their high charge (+2) and mass (4 amu) lose energy much faster than gamma rays. This loss of energy creates regions where the concentrations of H and OH radicals are much higher than with gamma radiolysis. Radical recombination reactions such as those forming H_2 are favored over such as those removing H_2 . Because the reaction removing H_2 is not as efficient, a steady state pressure is not attained. This phenomenon also occurs in the radiolysis of

liquid water where alpha radiolysis causes continuous H_2 production, and gamma radiolysis leads to very low steady state H_2 pressures.³ This similarity between H_2 production from concrete and water again suggests that the metal oxides of the concrete do not significantly alter the radiation chemistry of the water even though it is incorporated in the concrete. Another similarity is the higher value of $G(H_2)$ for alpha radiolysis. This higher value in water also results from the higher radical concentrations caused by alpha particles.

FIGURE 3
Pressurization
from Alpha
Radiolysis of
Concrete at 23°C

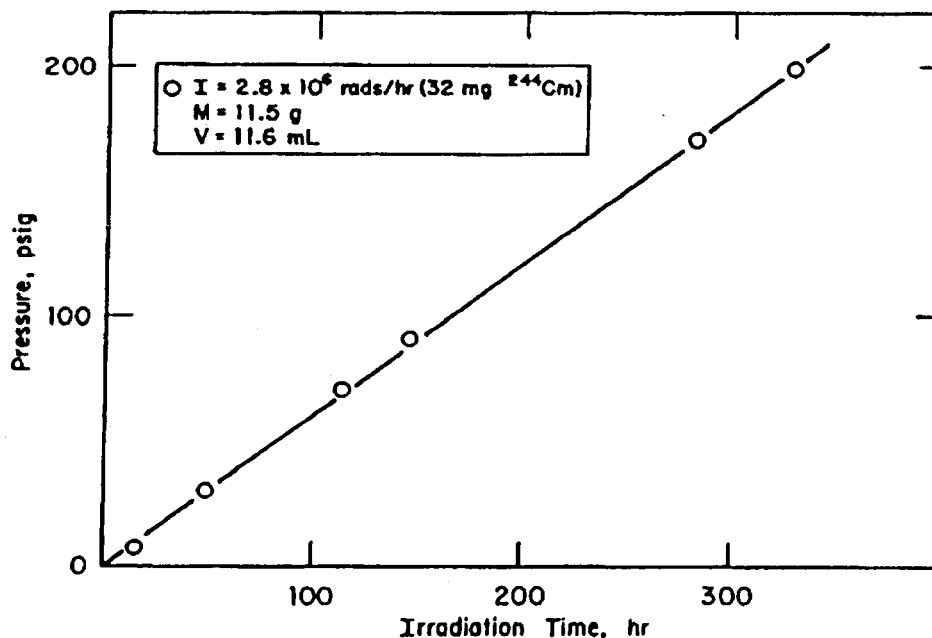
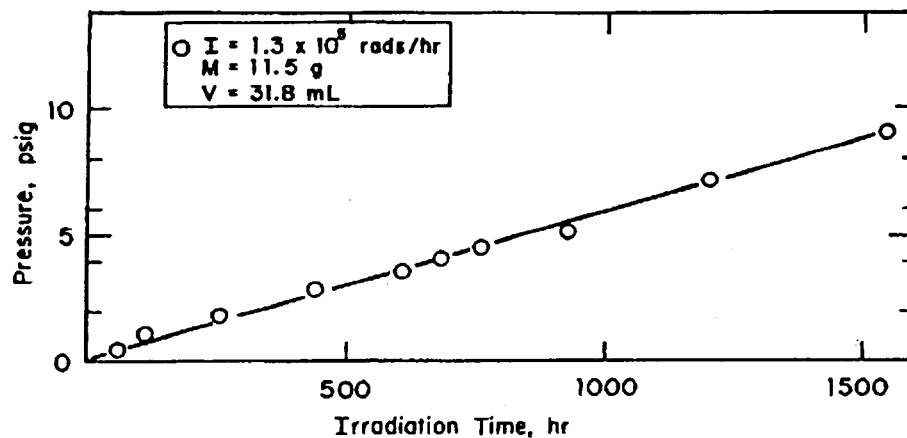


FIGURE 4
High Pressure
Generated from
Alpha Radiolysis
of Concrete at
23°C

Experimental Procedures

For the radiolysis tests, 6.5 g of the dry cement-plaster material was mixed in a steel test tube 0.9-cm ID by 10-cm long with 5 mL of 0.01M H_2SO_4 containing a known amount of ^{244}Cm . The amount of ^{244}Cm was determined by prior absolute alpha counting an aliquot of the solution. Also, prior to mixing, NO_3^- ions possibly present with the ^{244}Cm were destroyed by mild calcination of the ^{244}Cm . ^{244}Cm was redissolved with 0.01M H_2SO_4 because alpha radiolysis of NO_3^- ions produces O_2 ,¹¹ which might have led to additional pressurization from the concrete. After the concrete had cured for at least 16 hours, the tube was sealed to a pressure gauge and sampling valve. After the experiment, essentially all the gas was expanded into an evacuated sampler that was then removed from the glove box. The gas was analyzed by gas chromatography. The gas volume in the system containing the concrete was determined as in the gamma radiolysis tests.

GAMMA AND ALPHA RADIOLYSIS OF SOLIDIFIED ORGANIC WASTE FORM

The organic waste form irradiated was organic materials sorbed onto vermiculite. Vermiculite, a porous, highly absorptive mineral (hydrated magnesium-aluminum-iron silicate) is currently used for solidification of organic vacuum pump oils or organic cleaning solvent contaminated with tritium.¹ For this study, *Duo Seal** vacuum pump oil and research-grade n-octane were used. Usually, 2.5 mL of the organic material was sorbed onto each gram of vermiculite. For gamma radiolysis, the mixture was sealed in a steel irradiation container connected to a pressure gauge and sampling valve as in the concrete radiolysis tests. In the alpha radiolysis tests, ^{244}Cm , as an aqueous sulfate solution, was sorbed onto the vermiculite. The water was then evaporated by heating the vermiculite, and the organic material was added. This ensured that the ^{244}Cm was in direct contact with the vermiculite and organic material. The mixture was placed in a steel tube that was sealed to a pressure gauge and sampling valve.

Gamma Radiolysis Tests

Gamma radiolysis tests indicated that H_2 and small amounts of CO_2 and CH_4 were produced, N_2 was unaffected, and O_2 was consumed. In contrast to gamma radiolysis of concrete, steady state H_2 pressure was not attained. Also, the results indicated that only energy sorbed by the organic material produced H_2 . Energy sorbed by the vermiculite was not transferred to the organic material to produce H_2 . Finally, a slight dose rate dependence

* Trademark of Welch Scientific Company.

for $G(H_2)$ was observed. At low dose rates, the dependence vanished, and $G(H_2)$ based on energy sorbed only by the organic material was 4.6 molecules/100 eV for the octane and 2.0 for the vacuum pump oil.

Results and Discussion

Radiolytic pressurization at a dose rate of 1.4×10^7 rads/hr is shown in Figure 5. Clearly, a steady state pressure was not attained with either n-octane or vacuum pump oil. Gas analysis indicated that the evolved gas was nominally 96% H_2 , 3% CO_2 , and 1% CH_4 in each case. Approximately 50% of the O_2 was consumed in each test, and N_2 was unaffected. The G values for gas production were calculated from Equation 1 where M is now the mass of vermiculite and organic material irradiated. Results were 2.1 molecules/100 eV for n-octane and 1.2 for vacuum pump oil. G values for the individual gas components were obtained by multiplying the above G value times the fraction of that gas present.

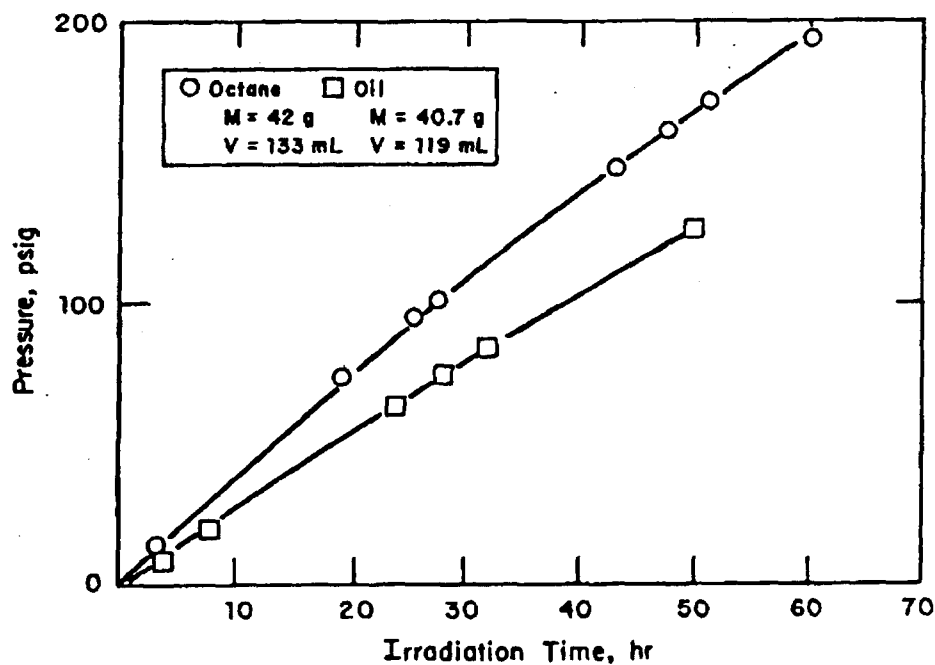


FIGURE 5. Pressurization from Gamma Radiolysis of Organic Material at 31°C

Tests at 1.4×10^7 rads/hr determined how the amount of organic material sorbed onto the vermiculite affected $G(H_2)$. The results (Figure 6) indicated that $G(H_2)$ was directly proportional to the amount of organic material present and predicted that radiolysis of dry vermiculite should produce no H_2 . This prediction was confirmed by irradiating vermiculite containing no organic. The linearity of the data in Figure 6 indicates that energy sorbed by the vermiculite does not cause the organic material to decompose to form H_2 . Similar results were obtained for the small yields of CO_2 and CH_4 .

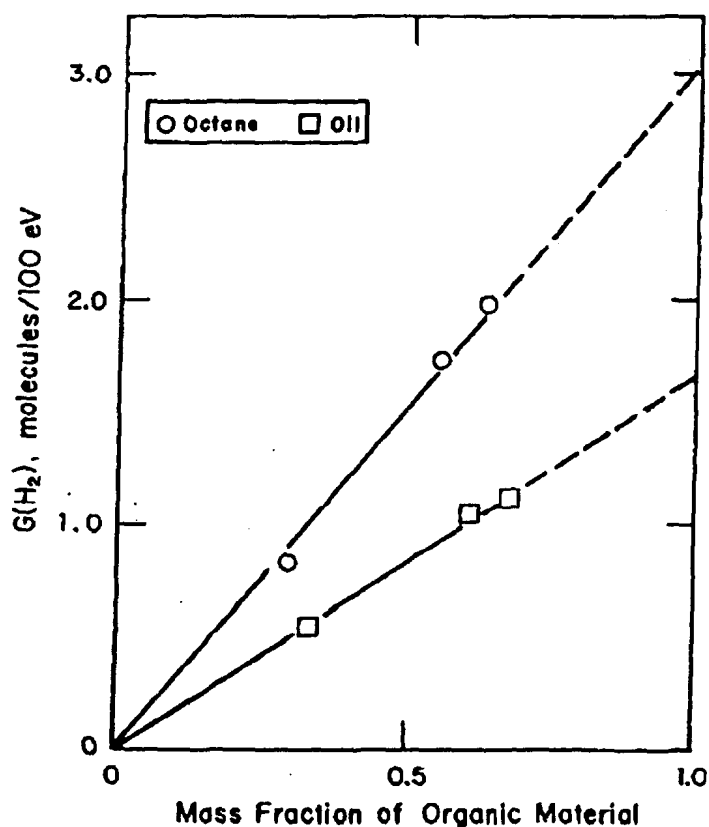


FIGURE 6. Dependence of $G(H_2)$ on Mass Fraction of Sorbed Organic Material

To determine the dose rate dependence of $G(H_2)$, samples were irradiated at lower dose rates (1.5×10^5 and 4.8×10^5 rads/hr). A typical result is shown in Figure 7. The initial pressure decrease was due to O_2 being consumed faster than H_2 was produced. The final gas composition was 23% H_2 , 73% N_2 , and 4% O_2 . Comparison of the partial pressures before and after radiolysis indicated that N_2 was unaffected and O_2 was ~80% consumed. $G(H_2)$ calculated from the final gas composition and total dose to the organic material (not the vermiculite) was 1.9 molecules/100 eV. Because H_2 was the only gas evolved in significant quantity, $G(H_2)$ could also be calculated from the final positive slope in Figure 7 and the dose rate. The result (1.8 molecules/100 eV) agrees with that calculated from the composition. The dose rate dependence for $G(H_2)$ (again based only on the energy sorbed by the organic material) for the oil and for n-octane is shown in Figure 8. The values at 1.4×10^7 rads/hr were obtained by extrapolating the data in Figure 6 to an organic mass fraction of 1.0. At low dose rates, the dose rate dependence of $G(H_2)$ vanished for both materials. The value of 4.6 molecules/100 eV for the sorbed n-octane agrees with the value obtained when pure liquid n-octane was irradiated.¹² This agreement indicates that sorption onto vermiculite does not significantly affect the radiation chemistry of the n-octane. Also, this agreement indicates, as do the data in Figure 6, that energy forming H_2 is not being transformed from vermiculite to the organic material.

The 100-eV consumption of O_2 [$G(-O_2)$] was calculated from the data in Figure 7. The molecules of O_2 consumed were calculated from the final gas composition. The dose necessary for this consumption was calculated from the dose rate and the time indicated in Figure 7 where pressure started to increase again. For the data in Figure 7, $G(-O_2)$ was 5.6 molecules/100 eV. In a test with n-octane, $G(-O_2)$ was 5.0 molecules/100 eV. Oxygen is consumed by reaction with radiolytically produced organic radicals on the vermiculite to form peroxides that eventually lead to aldehydes, ketones, or carboxylic acids. Oxygen was not completely consumed because it was apparently unable to diffuse from the pressure gauge, sampling valve, and associated tubing into the radiation field where it could react. In tests with the gauge and valve removed where nearly all the gas volume was in the radiation field, ~95% of the O_2 was consumed.

Another gamma radiolysis test was performed to determine whether a steady state H_2 pressure might result after complete O_2 consumption. At 1.4×10^7 rads/hr, an octane vermiculite sample was irradiated in an argon atmosphere. After 64 hours, the H_2 pressure was 200 psig and still increasing linearly indicating no approach to a steady state pressure. This pressure increase results from lack of a back reaction removing H_2 .

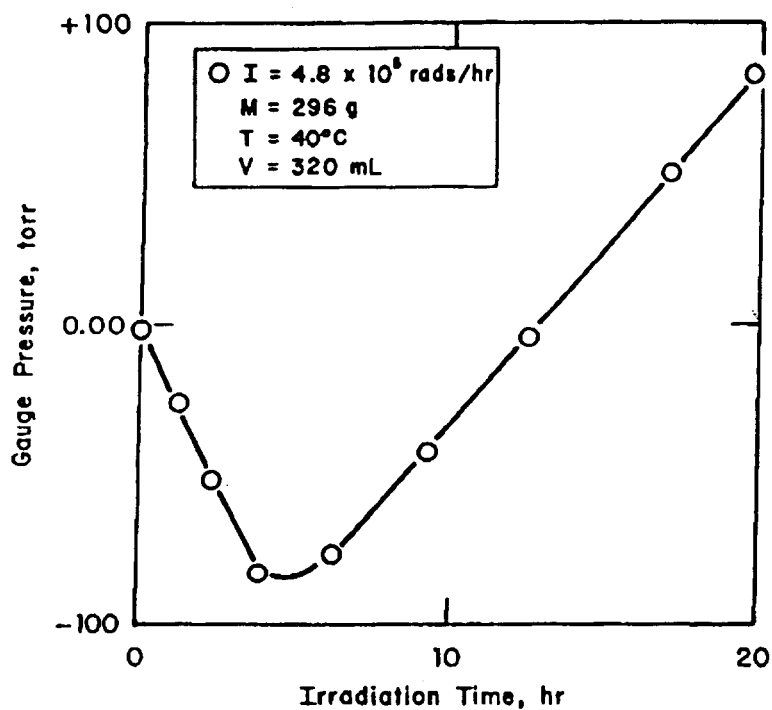


FIGURE 7. Pressurization from Gamma Radiolysis of Oil Sorbed onto Vermiculite

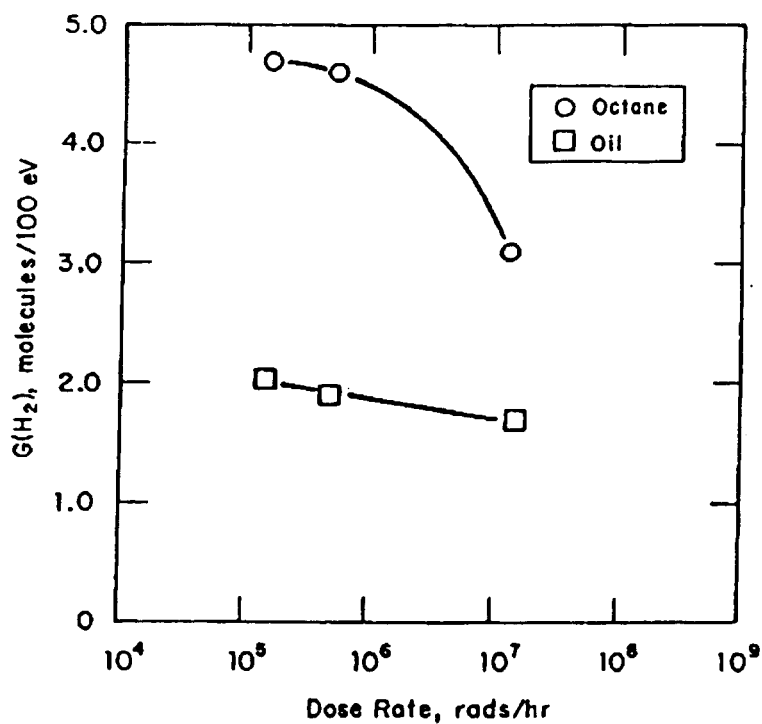


FIGURE 8. Dependence of $G(\text{H}_2)$ for Sorbed Organic Material on Gamma Dose Rate

Generally, the organic radicals ($R\cdot$) are not energetic enough to react with H_2 (Reaction 8); thus, a steady state is not attained.¹³



This test is in contrast to water radiolysis where a steady state is attained because of the reaction between OH and H_2 .

Experimental Procedures

For the tests at 1.4×10^7 rads/hr with the submerged ^{60}Co source, samples were irradiated in steel test tubes 20-cm long by 2.8-cm ID. Approximately 40 g of the mixture (2 g organic/g vermiculite) was placed in the tube, and the tube was sealed to a pressure gauge and sampling valve by ~ 25 ft of 0.1-cm-ID tubing. To decrease the volatilization of n-octane because of gamma heating during radiolysis, the tube was enclosed by coils for water cooling. For the tests with the ^{60}Co *Gammacell 220*, ~ 300 -g samples were irradiated in 500-cc bottles as with the concrete radiolysis tests. Dosimetry was performed with thin-film dosimeters⁸ or with the Fricke dosimeter.⁹ All other procedures were identical to those described for the concrete radiolysis tests.

Alpha Radiolysis Tests

Alpha radiolysis tests indicated that, as with gamma radiolysis, H_2 was the most significant product. Traces of CH_4 were also produced, and O_2 was consumed. For n-octane, $G(\text{H}_2)$ was 4.2 molecules/100 eV, nearly equal to the value found for gamma radiolysis (4.6). For the pump oil, $G(\text{H}_2)$ was 2.7, slightly higher than that obtained for gamma radiolysis (2.0).

Results and Discussion

Radiolytic pressure increases for two tests with n-octane containing 7.2 and 4.3 mg of ^{244}Cm are shown in Figure 9. At the end of the tests, gas composition for each was nominally 60% H_2 , 25% N_2 , 3% CH_4 , and 2% O_2 . Comparison of the partial pressures before and after radiolysis indicates that N_2 was unaffected and O_2 was 90% consumed. $G(\text{H}_2)$ values were calculated from the slopes in Figure 9, the dose rate (calculated from the amount of ^{244}Cm present), and the volume of gas produced. Based on energy sorbed by the organic material, $G(\text{H}_2)$ was 4.2 molecules/100 eV for the higher dose rate, and 4.3 for the lower, indicating no dose rate effect. Alpha radiolysis of the vacuum pump oil was

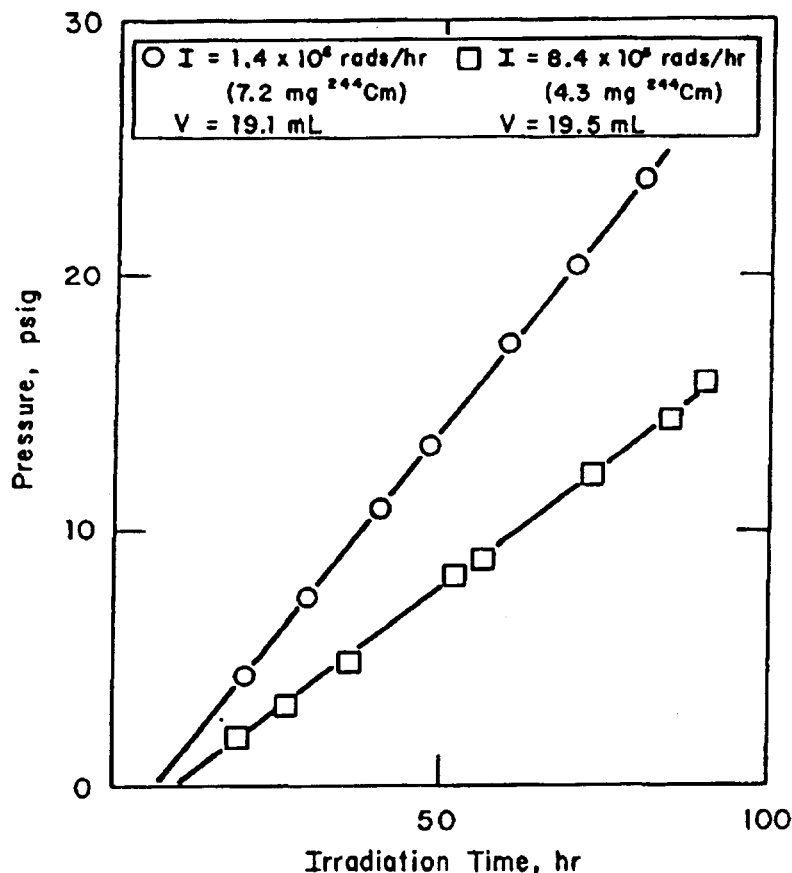


FIGURE 9. Pressurization from Alpha Radiolysis of Octane Sorbed onto Vermiculite at 23°C

studied at only one dose rate (Figure 10). Gas composition at the end of the test was 73% H₂, 25% N₂, 1% CH₄, and 0.7% O₂. O₂ was 94% consumed, and N₂ was not affected by radiolysis. G(H₂) was 2.7 molecules/eV.

Experimental Procedures

The irradiation containers were identical to those used in alpha radiolysis tests of the concrete samples (page 10). In these tests, 2.9 g of organic material was sorbed onto 2.3 g of vermiculite. A known amount of ²⁴⁴Cm in an aqueous solution was sorbed onto the vermiculite. The water was then removed by heating the mixture to a constant weight. The organic material was then added, and the mixture was sealed in the steel tube with a pressure gauge and sampling valve. After the test, the gas was sampled and analyzed as in the concrete alpha radiolysis tests.

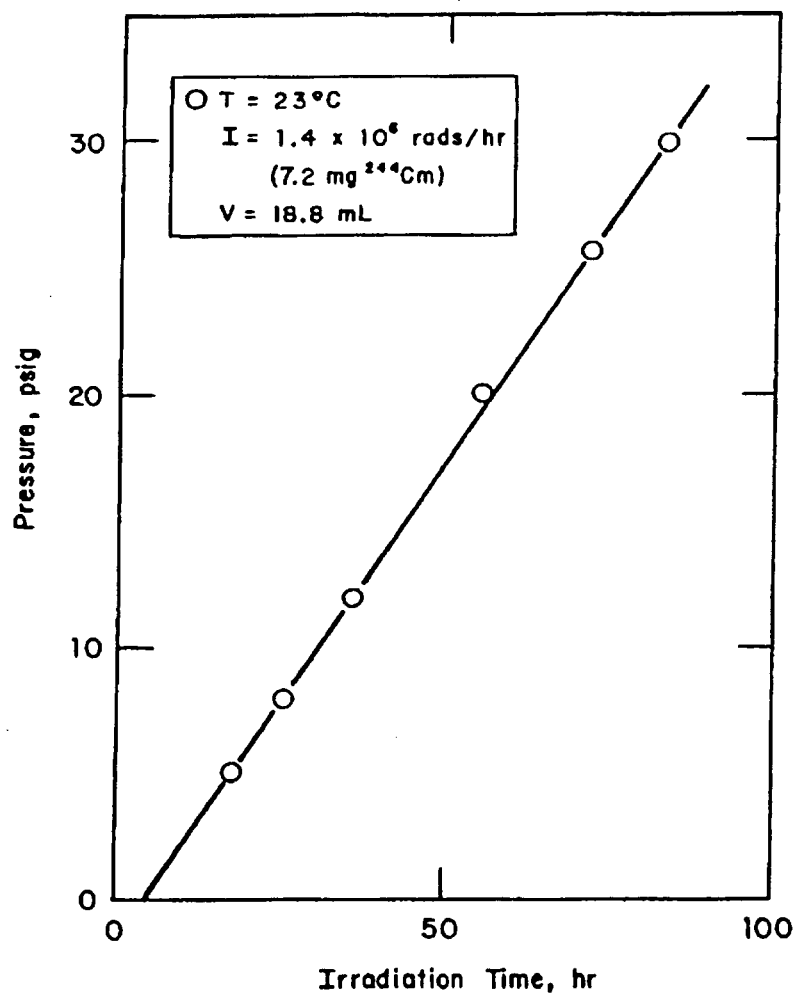


FIGURE 10. Pressurization from Alpha Radiolysis of Vacuum Pump Oil Sorbed onto Vermiculite

ESTIMATION OF $G(H_2)$ FOR TRITIUM BETA RADIOLYSIS

$G(H_2)$ for 3H beta radiolysis can be estimated from the $G(H_2)$ values for alpha and gamma radiolysis. Radiolytic products formed by the three types of radiation are expected to be identical because all three transfer energy to electrons of the material irradiated. These energetic electrons then cause chemical degradation to the material. Because of the different LET values of the radiations, products may be formed with different 100-eV yields. For example, with the concrete, $G(H_2)$ was 0.03 molecule/100 eV for gamma radiolysis and 0.6 for alpha radiolysis. Similarly, for liquid water, $G(H_2)$ is 0.5 for gamma radiolysis and 1.6 for alpha radiolysis.³ This difference results from different spatial distribution of intermediates formed by the radiations. In water, LET values for ^{60}Co gamma, 3H beta, and ^{244}Cm alpha radiations are 0.02, 0.36, and 8.8 eV/A°, respectively.⁵ Although these parameters have not been determined in concrete or vermiculite, their relative values, 1.0, 18, and 440 are probably reasonably invariant from system to system. Therefore, $G(H_2)$ for 3H beta radiolysis was estimated for each waste form from plots of $G(H_2)$ versus relative LET values.

$G(H_2)$ for Concrete Waste

In Figure 11, the two values for $G(H_2)$ for concrete radiolysis are plotted along with data for $G(H_2)$ from liquid water for comparison. The dashed line is a linear interpolation of the concrete data and suggests that $G(H_2)$ for 3H -beta radiolysis is 0.3 molecule/100 eV. By following the curvature of the data for liquid water, 0.1 is estimated. This estimate may be closer to the true value because H_2 is probably formed in the two systems by the same mechanism (recombination of H atoms). However, until radiolysis experiments are performed with 3H beta rays, the estimate for $G(H_2)$ has to be 0.1 to 0.3 molecule/100 eV.

$G(H_2)$ for Solidified Organic Waste

The effect of LET on $G(H_2)$ is much less in radiolysis of the organic materials sorbed onto vermiculite (Figure 12). The values for ^{60}Co gamma radiolysis were calculated at the low dose rates. Because of this smaller effect of LET, values for 3H beta radiolysis can be estimated more accurately. For the n-octane, 4.4 molecules/100 eV is estimated; for the vacuum pump oil, 2.2 is estimated. These values were used to estimate radiolytic pressurization of containers of tritiated waste.

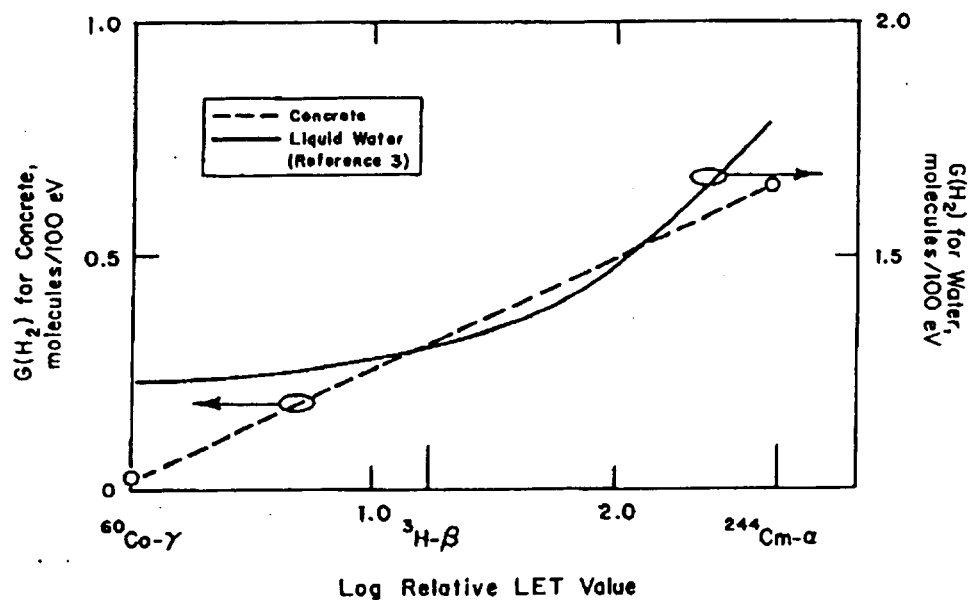


FIGURE 11. Effect of Linear Energy Transfer on $G(H_2)$ from Radiolysis of Concrete and Liquid Water

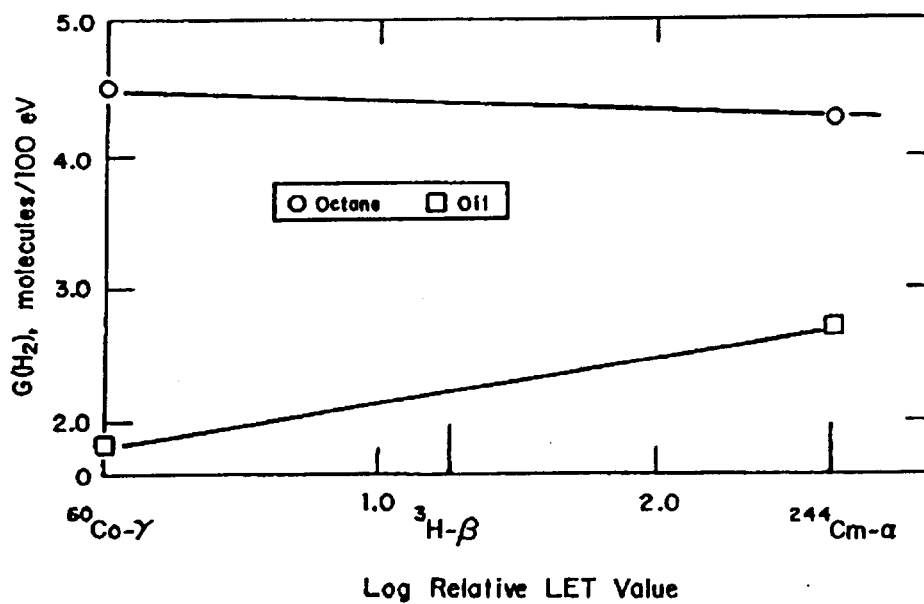


FIGURE 12. Effect of Linear Energy Transfer on $G(H_2)$ from Radiolysis of Octane or Vacuum Pump Oil Sorbed onto Vermiculite

RADIOLYTIC PRESSURIZATION IN TRITIATED WASTE CONTAINERS

For long-term storage of tritium waste, the solidified material is sealed in an appropriate primary container such as a metal or polyethylene drum.¹ This drum is then sealed in a metal drum that is, in some cases, sealed in another metal drum. From results of this study, pressurization rates and pressures in the primary drums can be estimated as a function of storage time if the tritium content and gas volume in the drums are known.

Pressurization from Tritiated Concrete Waste

Because of H₂ production, containers of tritiated concrete will pressurize. However, because of O₂ depletion, the rate of total pressurization will be less than that of H₂ pressurization alone. Initially, the H₂ pressurization rate is linear and is given by

$$\frac{dP_{H_2}}{dT} = \frac{RT}{NV} \cdot \frac{G(H_2)}{100} \cdot \frac{dE}{dt} \quad (9)$$

where

R = gas constant, psi liter/mole °K

T = temperature, °K

N = Avogadro's number, molecules/mole

V = gas volume in the container

G(H₂) = 0.1 to 0.3 molecule/100 eV

$\frac{dE}{dt}$ = dose rate from ³H beta decay, eV/day

The dose rate is given by

$$\frac{dE}{dt} = \frac{3.7 \times 10^{10} \text{ dis}}{\text{sec Ci}} \cdot \frac{8.6 \times 10^4 \text{ sec}}{\text{day}} \cdot Ci_t \cdot \bar{E} \quad (10)$$

where

Ci_t = curies of ³H present

\bar{E} = average energy per beta particle, 5.69 keV¹⁴

Because of the radioactive decay of ^3H , $\text{Ci}_t = \text{Ci}_t^0 e^{-\lambda t}$ where Ci_t^0 is the initial amount of ^3H present and λ is its decay constant ($1.5 \times 10^{-4} \text{ day}^{-1}$).¹⁵ Equation 9 then becomes

$$\frac{dP_{\text{H}_2}}{dt} = \frac{RT}{NV} \cdot \frac{G(\text{H}_2)}{100} \cdot \frac{1.8 \times 10^{19} \text{ eV}}{\text{Ci} \cdot \text{day}} \cdot \text{Ci}_t^0 e^{-\lambda t} \quad (11)$$

Integrating Equation 11 gives P_{H_2} as a function of time

$$P_{\text{H}_2} = \frac{RT}{NV} \cdot \frac{G(\text{H}_2)}{100} \cdot \frac{1.8 \times 10^{19} \text{ eV}}{\text{Ci}_t \text{ day}} \cdot \frac{\text{Ci}_t^0}{\lambda} \cdot (1 - e^{-\lambda t}) \quad (12)$$

As the H_2 pressure increases in the container, the rate of H_2 pressurization decreases. This pressure decrease has been established for ^3H beta radiolysis by data obtained at another laboratory* where a sample of solidified aqueous waste (tritiated water sorbed onto vermiculite) was sealed in a steel container. The pressure in the container initially increased, but eventually attained a steady state (Figure 13). At steady state, the H_2 pressure based on gas composition was 11 psi. The remainder of the gas was N_2 and O_2 along with traces of He and D_2 . The dose rate in the waste ($9 \times 10^4 \text{ rads/hr}$) was estimated from the tritium content of the waste ($1.7 \times 10^5 \text{ Ci}$) and its mass (14 kg water on 18 kg vermiculite).¹⁶ When a similar mixture of water and vermiculite was gamma-irradiated at this dose rate at SRP, the steady state H_2 pressure was $9 \pm 2 \text{ psi}$, in reasonable agreement with that obtained by ^3H beta radiolysis. This agreement indicates that ^3H beta radiolysis effects can be simulated by ^{60}Co gamma radiolysis and that the steady state H_2 pressure in waste containers can be estimated from Figure 2, if the dose rate to the waste is known. At $9 \times 10^4 \text{ rads/hr}$, a steady state pressure of 14 psi predicted for the concrete is reasonably close to the 11 psi calculated for the water-vermiculite mixture. This agreement suggests that aqueous concrete and vermiculite waste have nearly equal steady state pressures and is to be expected if the oxide solidification matrices do not affect the radiation chemistry of H_2O significantly.

The amount of pressurization in a conceptual waste container will now be estimated. The assumed container is a 27-gallon drum containing 10^5 Ci of tritium solidified in 20 gallons of concrete. The void volume is 7.1 gallons (27 liters) if the concrete is assumed to have a 10% porosity. The initial H_2 pressurization

* Letter from D. R. Storey, Monsanto Research Corporation, Miamisburg, Ohio, to R. L. Wainwright, USAEC, Miamisburg, Ohio, June 24, 1974.

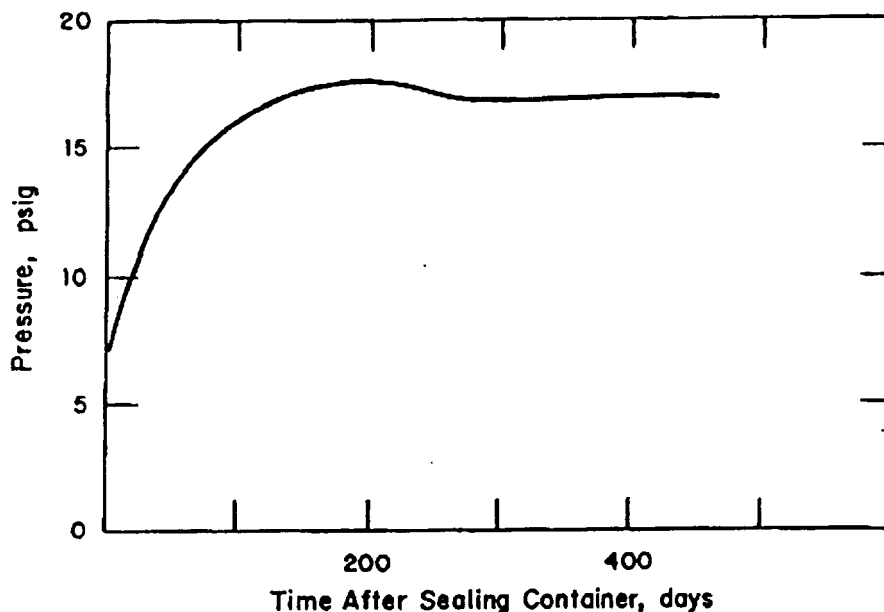


FIGURE 13. Pressurization from ^3H - β Radiolysis of Water Sorbed onto Vermiculite (Data obtained from D. R. Storey, Monsanto Research Corporation, Miamisburg, Ohio, June 24, 1974)

rate at 23°C calculated from Equation 11 is 0.04 to 0.12 psi/day depending on the choice for $G(\text{H}_2)$ (0.1 or 0.3 molecule/100 eV). At these rates, the gaseous mixture will become flammable (0.4% H_2 or 0.6 psi H_2)¹⁷ in approximately 6 to 15 days assuming no O_2 depletion. Because of this depletion, however, longer times will be necessary. In this container, the dose rate is 1.6×10^4 rads/hr if a density of 1 kg/L is assumed for the concrete. From Figure 2, a steady state H_2 pressure of <10 psi is predicted.

Pressurization from Tritiated Organic Waste

H_2 pressurization rates from n-octane or vacuum pump oil sorbed on vermiculite are given by

$$\frac{dP_{\text{H}_2}}{dt} = \frac{RT}{NV} \cdot \frac{G(\text{H}_2)}{100} \cdot \frac{dE}{dt} \cdot X \quad (13)$$

X is the mass fraction of organic material present, and $G(\text{H}_2)$ is based on 100-eV energy sorbed by the organic material. The term $(dE/dt)X$ is the dose rate to the organic material. A better estimate of this dose rate would be based on the electron fraction of organic material because alpha, beta, and gamma radiations primarily transfer energy to the electrons of a system.¹⁸ Using

the mass fraction introduces an error of <10% that is considered not significant in these pressure estimations. Relating dE/dt to the initial curies of 3H present and integrating Equation 11 give

$$P_{H_2} = \frac{RT}{NV} \cdot \frac{G(H_2)X}{100} \cdot \frac{Ci_t \cdot I}{\lambda} (1 - e^{-\lambda t}) \quad (14)$$

where

$$I = 1.8 \times 10^{19} \text{ eV/Ci} \cdot \text{day}$$

Both the gamma and alpha radiolysis data indicate that a significant back reaction for H_2 does not occur with the organic material. This indicates that Equation 14 may be valid as long as organic material and 3H are present. On this basis, the pressure of H_2 after decay of all the 3H has decayed is given by

$$P_{H_2}(\text{final}) = \frac{RT}{NV} \cdot \frac{G(H_2)X}{100} \cdot \frac{Ci_t \cdot I}{\lambda} \quad (15)$$

The pressure of O_2 as a function of time is given by

$$P_{O_2} = P_{O_2}^0 - \frac{RT}{NV} \cdot \frac{G(-O_2)X}{100} \cdot \frac{Ci_t \cdot I}{\lambda} \cdot (1 - e^{-\lambda t}) \quad (16)$$

where $P_{O_2}^0$ is nominally 3 psi. The gamma and alpha radiolysis data indicate that eventually O_2 will be essentially depleted from the gas phase. CH_4 and CO_2 will also be produced, but their contribution to the total pressure will be negligible.

The pressurization from tritiated organic solvent sorbed onto vermiculite in a conceptual waste container will now be estimated. The container is a 27-gallon drum containing 10^4 Ci of tritium in 7.4 gallons of octane or vacuum pump oil sorbed onto 20 gallons of vermiculite. With 0.7 g/mL as the density of the organic material and 0.15 as the bulk density of vermiculite (estimated at SRL), the radiation dose rate is 5400 rads/hr. The mass fraction organic material is 0.64 and the void volume is 69 liters (with 2.3 g/mL as the crystal density of the vermiculite). $G(H_2)$ values for octane and pump oil are 4.4 and 2.2 molecules/100 eV, respectively (Figure 12). The initial pressurization rates are 0.044 and 0.02 psi/day, respectively, for octane and pump oil. If no depletion in O_2 is assumed, the mixtures become flammable in 14 and 7 days, respectively. With O_2 depletion, these times become longer. Eventually, the O_2 will be essentially all consumed. The final pressures of H_2 for the two materials are 310 psi for the octane and 155 psi for the vacuum pump oil. With larger amounts of tritium, larger final pressures would be generated.

REFERENCES

1. T. B. Rhinehammer and E. A. Mershad. "Techniques and Facilities for Handling and Packaging Tritiated Liquid Wastes for Burial." p 1067 in *Proceedings of the Second AEC Environmental Protection Conference, Albuquerque, NM, April 16, 1974*. USAEC Report WASH-1332(74) (Vol. 2) (1974).
2. J. A. Franz and L. L. Burger. *Polymeric Media for Tritium Fixation*. USERDA Report BNWL-B-430, Battelle Pacific Northwest Laboratories, Richland, WA (1975).
3. I. G. Draganić and Z. D. Draganić. *The Radiation Chemistry of Water*. Academic Press, New York, NY (1971).
4. A. J. Swallow. *Radiation Chemistry of Organic Compounds*. Pergamon Press, New York, NY (1960).
5. E. J. Henley and E. R. Johnson. *The Chemistry and Physics of High Energy Reactions*. p 254, University Press, Washington, DC (1969).
6. N. E. Bibler. *Radiolytic Gas Production from Concrete Containing Savannah River Plant Waste*. USERDA Report DP-1464, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, SC (to be issued).
7. W. G. Burns and R. Barker. "Dose Rate and Linear Energy Transfer Effects in Radiation Chemistry." p 305 in *Progress in Reaction Kinetics, Vol. 3*, Pergamon Press, New York, NY (1965).
8. N. E. Bibler. *Calibration of Intense ^{60}Co Gamma Ray Sources at the Savannah River Plant*. USERDA Report DP-1414, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken SC (1976).
9. H. Fricke and E. J. Hart. p 185 in *Radiation Dosimetry, Vol. 2* (2nd Edition). F. H. Attix and W. C. Roesch, editors. p 185, Academic Press, NY (1966).
10. C. Kellar. *The Chemistry of the Transuranium Elements*. p 530, Verlag Chemie GmbH, Weinheim, West Germany (1971).

11. N. E. Bibler. "Curium-244 α Radiolysis of Nitric Acid. Oxygen Production from Direct Radiolysis of Nitrate Ions." *J. Phys. Chem.* 78, 211 (1974).
12. H. A. Dewhurst. "Radiation Chemistry of Organic Compounds. I. n-Alkane Liquids." *J. Phys. Chem.* 61, 1466 (1957).
13. J. W. T. Spinks and R. J. Woods. *An Introduction to Radiation Chemistry* (2nd edition). p 360, John Wiley and Sons, New York, NY (1976).
14. W. L. Pillinger, J. J. Hentges, and J. A. Blair. "Tritium Decay Energy." *Phys. Rev.* 121, 232 (1961).
15. K. C. Jordan, B. C. Blanke, and W. A. Dudley. "Half-Life of Tritium." *J. Inorg. Nucl. Chem.* 29, 2129 (1967).
16. J. W. T. Spinks and R. J. Woods. *An Introduction to Radiation Chemistry* (2nd edition). p 115, John Wiley and Sons, New York, NY (1976).
17. H. F. Coward and G. W. Jones. "Limits of Flammability of Gases and Vapors." p 15 in *Bulletin 503, Bureau of Mines*. U. S. Government Printing Office, Washington, DC (1952).
18. R. C. Weast (editor-in-chief). *Handbook of Chemistry and Physics* (51st edition). p B-197, The Chemical Rubber Company, Cleveland, OH (1971).



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June 27, 1977

Mr. A. F. Westerdahl, Chief
Patent Branch
Savannah River Operations Office
Energy Research and Development
Administration
Aiken, South Carolina 29801

Dear Mr. Westerdahl:

REQUEST FOR PATENT REVIEW

Please review for patent matter:

DP-1459, "Radiolytic Gas Production From Tritiated Waste Forms; Gamma and Alpha Radiolysis Studies" by Ned E. Bibler and E. G. Orebaugh.

If any technical clarification is needed please call H. S. Hilborn, whose Document Review is attached.

Please telephone your comments to the TIS office (ext. 3598) and notify me by signing and returning to TIS the original of this letter. A copy is provided for your file.

If you decide to pursue a patent on any development covered, I shall be happy to supply additional information required such as appropriate references and the names of persons responsible for the development.

Very truly yours,

R. E. Naylor, Director
Technical Division

The above item is approved for release.

A. F. Westerdahl
A. F. Westerdahl
Chief, Patent Branch
ERDA-SR

Date 7/5/77

By: H. S. Hilborn

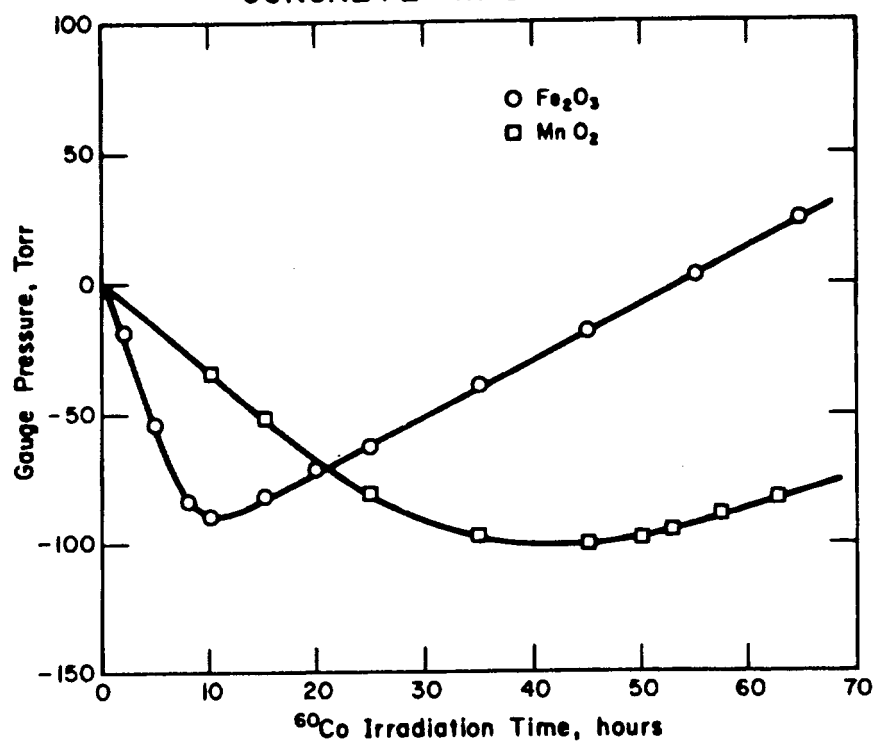
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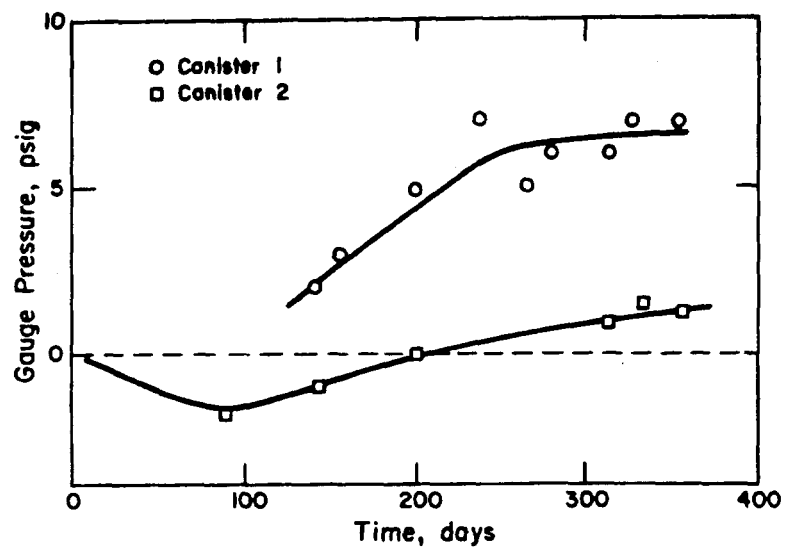
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LOW DOSE RATE γ -RADIOLYSIS OF CONCRETE WASTE FORMS

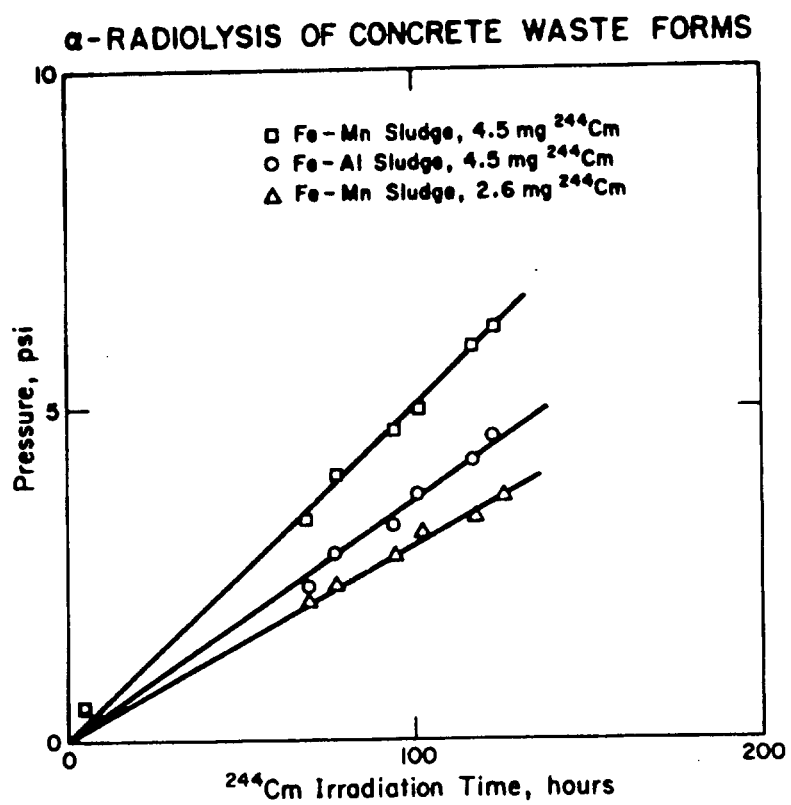


SLIDE 6. Low Dose Rate Radiolysis of Concrete and Fe_2O_3 or MnO_2 as Simulated Waste

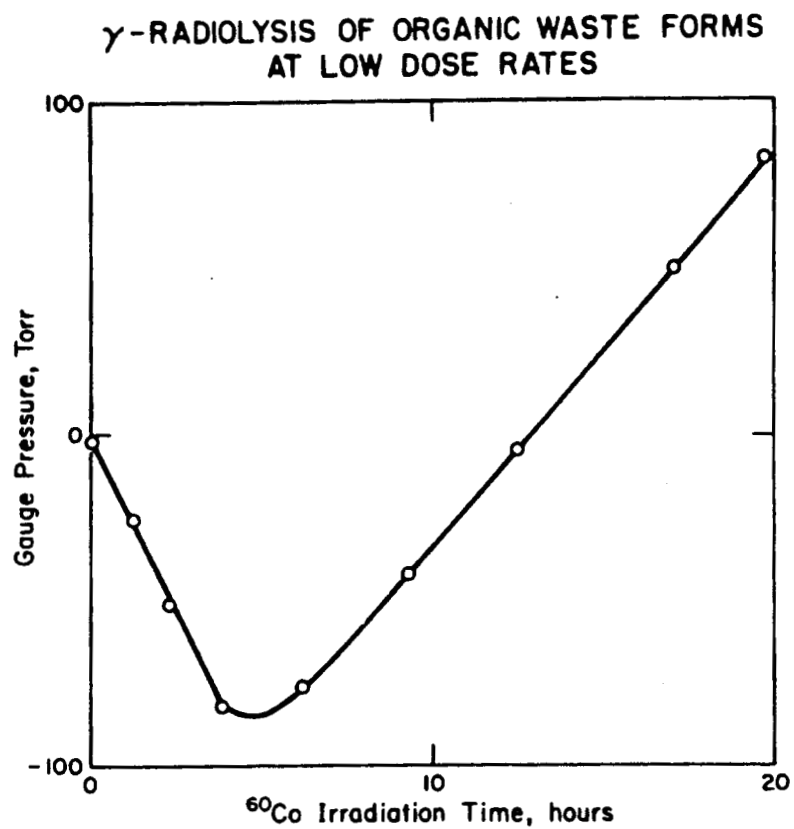
CANISTER PRESSURIZATION FROM RADIOACTIVE CONCRETE WASTE FORMS



SLIDE 7. Radiolytic Pressurization of Concrete and
SRP Radioactive Waste

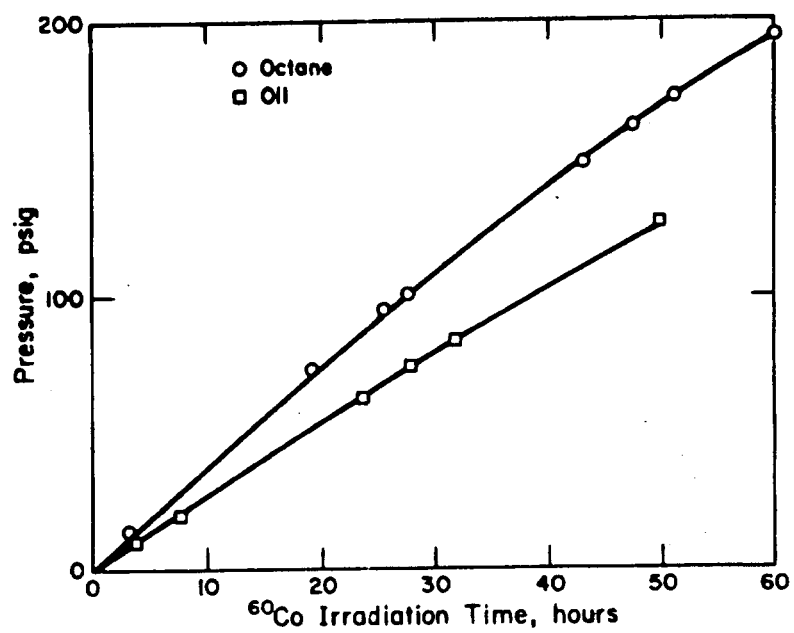


· SLIDE 8. Alpha Radiolysis of Concrete and SRP Simulated Waste

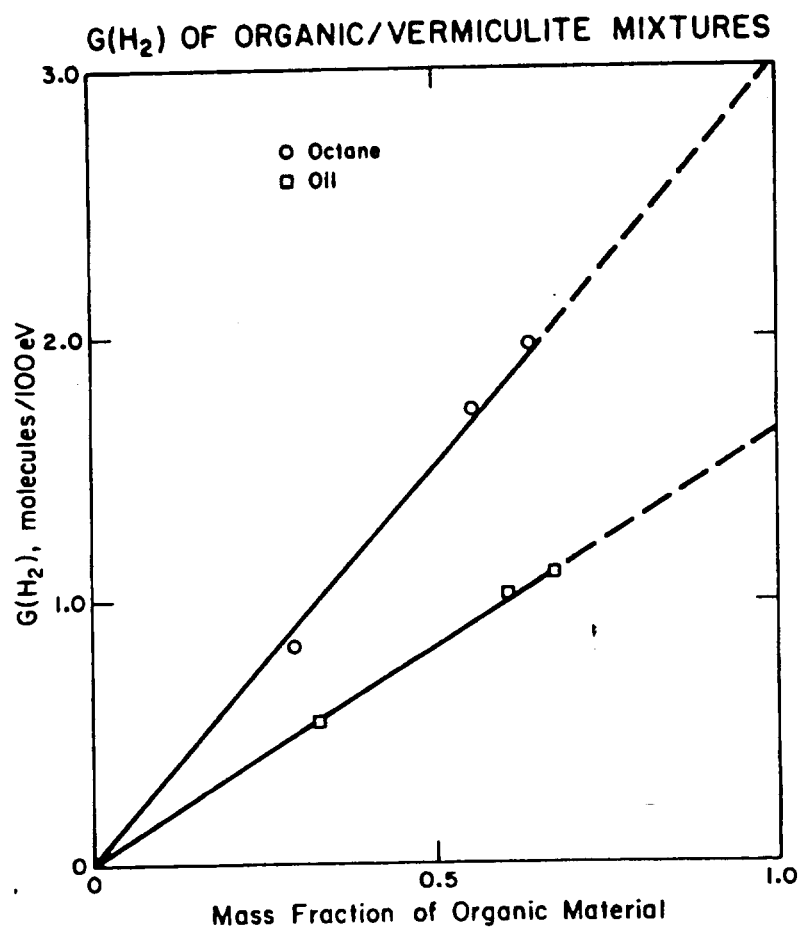


SLIDE 9. Low Dose Rate Gamma-Radiolysis of Pump Oil
Sorbed on Vermiculite

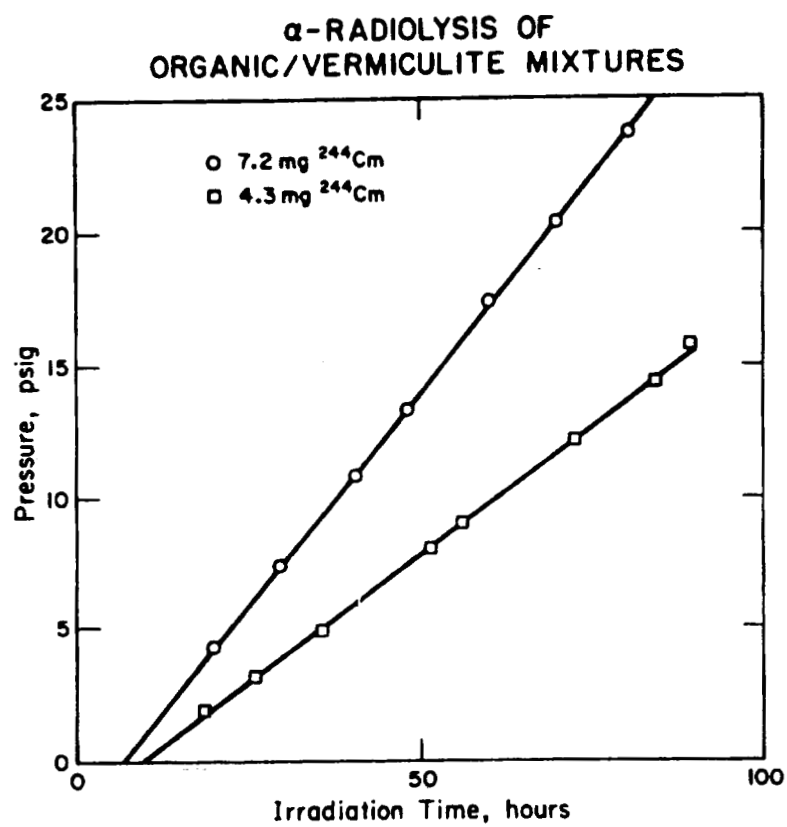
**γ -RADIOLYSIS OF ORGANIC WASTE FORMS
AT HIGH DOSE RATES**



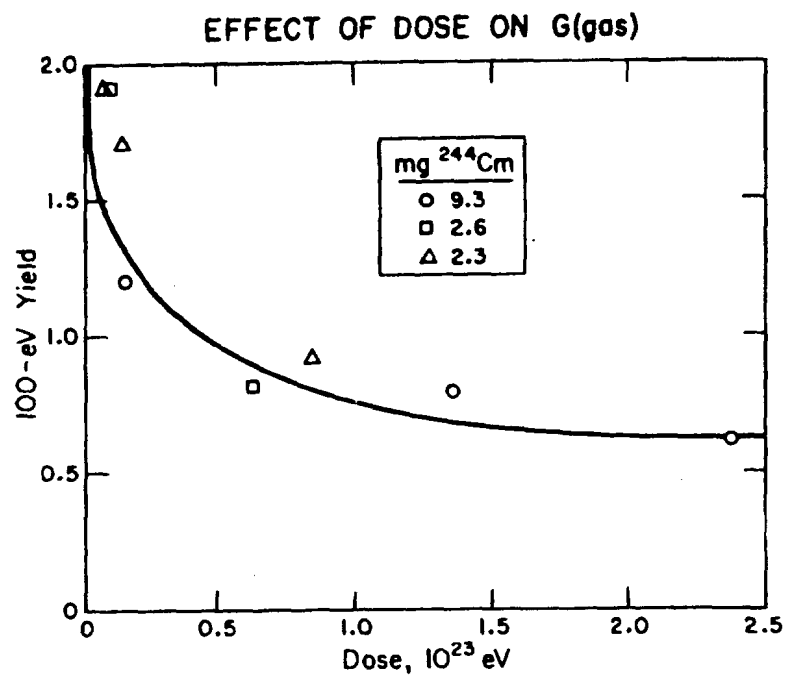
SLIDE 10. High Dose Rate Gamma-Radiolysis of Octane or Pump Oil Sorbed on Vermiculite



SLIDE 11. Effect of Organic/Vermiculite Ratio on G(H₂)

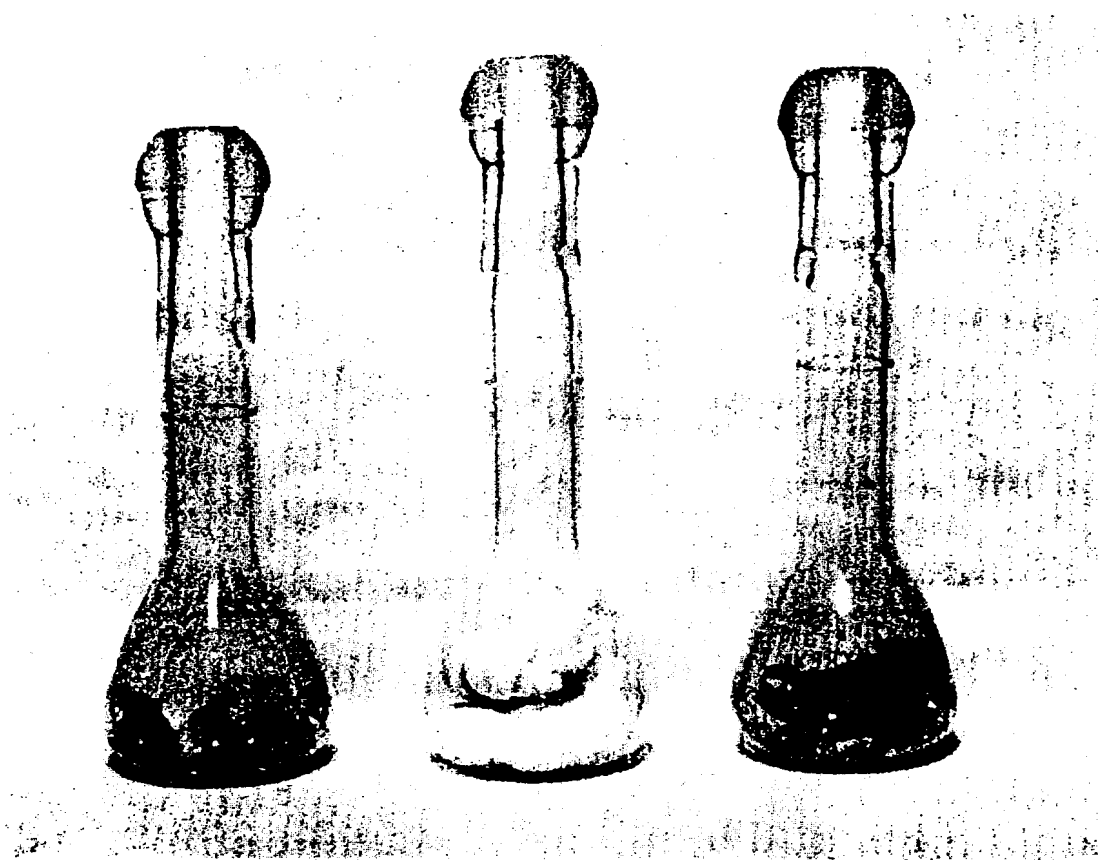


SLIDE 12. Alpha Radiolysis of Octane Sorbed on Vermiculite



SLIDE 14. Effect of Dose on the 100-eV Yield for Gas Production

DEGRADED CELLULOSE FROM α -RADIOLYSIS



SLIDE 15. Physical Damage to Cellulose from Alpha-Radiation

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RADIOLYTIC GAS PRODUCTION DURING
LONG-TERM STORAGE OF NUCLEAR WASTES

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by

Ned E. Bibler

Savannah River Laboratory
E. I. du Pont de Nemours and Company
Aiken, South Carolina

A paper accepted for presentation at the 28th
*Southeastern Regional Meeting of the American
Chemical Society* to be held in Gatlinburg,
Tennessee, on October 27-29, 1976.

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RADIOLYTIC GAS PRODUCTION DURING
LONG-TERM STORAGE OF NUCLEAR WASTES*

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Aiken, SC 29801

ABSTRACT

Gases produced by *in situ* radiolysis of sealed solidified nuclear wastes during long-term storage could conceivably breach containment. Therefore, candidate waste forms (matrices containing simulated nuclear wastes) were irradiated with ^{60}Co - γ and ^{244}Cm - α radiation. These forms were: cement containing simulated fission product sludges, vermiculite containing organic liquids, and cellulose contaminated with α -emitting transuranic isotopes. For cement waste forms exposed to γ -radiolysis, an equilibrium hydrogen pressure was reached that was dose rate dependent. For α -radiolysis, equilibrium was not reached. With organic wastes (n-octane on vermiculite), H_2 and traces of CO_2 and CH_4 were produced, and O_2 was consumed with both radiations. Only energy absorbed by the organic material was effective in producing H_2 . At low dose rates with both α - and γ -irradiations, $G(\text{H}_2)$ was 4.5 and $G(-\text{O}_2)$ was 5.0. Also, equilibrium was not obtained. For cellulosic material, H_2 , CO_2 , and CO were produced in the ratio

* Work done under USERDA Contract No. AT(07-2)-1.

of 1.0:0.7:0.3, and O₂ was consumed. With α -radiolysis, G(gas) was dose dependent; measured values ranged from 2.2 to 0.6 as the dose increased. Implications of all these results on long-term storage of radioactive waste will be discussed. Some data from an actual nuclear waste form will also be presented.

INTRODUCTION

Much effort is being expended in many laboratories to develop methods of solidifying and storing nuclear wastes to isolate them from the environment. These wastes are primarily fission products or alpha-emitting transuranic isotopes dissolved in aqueous or organic solutions or sorbed on laboratory wastes such as tissues or other cellulosic materials. In nearly all the proposed storage methods, the solidified waste is sealed in a primary, secondary, and sometimes a tertiary steel container. One property of the solidified form that has to be evaluated is the production of gases from *in situ* radiolysis of the form. If sufficient gases are produced, they may pressurize the containers, and containment could be breached.

At the Savannah River Laboratory, we have measured radiolytic gas production from three types of solidified wastes: fission product sludges incorporated in concrete, contaminated organic wastes sorbed on vermiculite, and cellulosic material contaminated with alpha-emitting isotopes.

CONCRETE WASTE

One method being evaluated for solidifying high level radioactive waste sludges from the Savannah River Plant (SRP) is to mix them with cement to form concrete.¹ Nominal composition of the preferred cement and the washed dried sludge is shown in SLIDE 1. In the final waste form, the sludge-to-cement ratio will be 0.67. As indicated in SLIDE 1, most of the initial radiation in the sludge will be beta-gamma from decay of ^{90}Sr and its daughter and ^{137}Cs . Alpha radiation will be present from decay of ^{238}Pu and ^{239}Pu .

SLIDE 2 shows the time-dependence of the calculated radiation dose rates to the form based on the data on SLIDE 1. Integrated doses are shown in SLIDE 3. In these calculations, it was assumed that all alpha, beta, and gamma radiation was absorbed by the form. As indicated in SLIDE 3, the final doses are quite large. SLIDE 4 shows pressurization produced by ^{60}Co gamma-irradiation of a sealed canister of concrete containing Fe_2O_3 to simulate sludge. The ^{60}Co gamma radiation simulates beta-gamma radiation from ^{90}Sr and ^{137}Cs . The only gas produced in significant amounts was hydrogen, which reached an equilibrium pressure that depended on the dose rate. SLIDE 5 shows the effect of dose rate on this equilibrium pressure for the Fe_2O_3 -concrete form as well as neat cement and concrete containing MnO_2 , another material found in SRP sludges. This dose rate effect is consistent with a model in which molecular hydrogen is formed by recombination of hydrogen atoms and removed by reaction

with hydroxyl radicals. These reactions occur in the radiolysis of liquid water.² Extrapolation of the data to the calculated dose rate for actual waste indicates that for irradiation times of a few hundred years, during which radiolysis is primarily due to decay of ^{90}Sr and ^{137}Cs , hydrogen will reach an equilibrium pressure between 8 and 28 psi. Other experiments showed that this equilibrium pressure is independent of the gas volume.

While hydrogen was being produced at low dose rates, oxygen that was present in the canister was consumed. The effect of this oxygen consumption on the radiolytic pressurization is shown in SLIDE 6. Analyses of gases from two irradiations show oxygen consumption of 75 and 95%, respectively. Nitrogen was unaffected. This implies that in the containers of waste concrete, oxygen will be completely consumed. Oxygen consumption is attributed to reaction of oxygen with radiolytic hydrogen atoms to form hydroperoxy (HO_2) radicals that recombine to form hydrogen peroxide (H_2O_2). Evidence for this compound was obtained by treating the irradiated concrete with aqueous iodide (I^-) solution or ferricyanide [$\text{Fe}(\text{CN})_6^{3-}$] solution.

Pressurization data for two samples of concrete and actual SRP waste are shown in SLIDE 7. The results are consistent with those from gamma-radiolysis of concrete and simulated waste. The equilibrium pressure range predicted from gamma-radiolysis of simulated waste and the radioactivity present in this material was between 4 and 22 psi. The observed equilibrium pressure of 6 to 7 psi is within this range.

The effect of ^{244}Cm alpha-radiolysis on concrete and simulated waste is shown in SLIDE 8. With alpha-radiolysis, oxygen is a product, composing 25% of the evolved gas. Again, nitrogen was not affected. Experiments at larger doses indicated that, unlike gamma radiolysis, hydrogen production by alpha radiolysis is not affected by hydrogen pressures up to 200 psi. In the waste containers, alpha-radiolysis will predominate after the decay of ^{137}Cs and ^{90}Sr , about 200 years. Even though the alpha dose rate from the ^{239}Pu is low in the waste form (~ 7 rads/hr), hydrogen may accumulate to a final pressure as high as 1600 psi after $\sim 10^5$ years. The oxygen pressure may reach 300 psi.

All of the above results are consistent with established free radical mechanisms for radiolytic destruction of water. In application, the results suggest that radiolytic pressurization in containers of concrete and SRP waste will be low for the first several hundred years storage.

ORGANIC SOLVENT WASTES SORBED ON VERMICULITE

A method being evaluated for treating contaminated organic solvents is to sorb them on vermiculite and then seal this material in steel drums for storage.³ For this type of waste, radiolytic pressurization data were obtained by gamma- and alpha-irradiation of octane or a commercial vacuum pump oil on vermiculite. Results of high and low dose rate gamma-radiolysis experiments are shown in SLIDES 9 and 10. As with concrete, oxygen was consumed, nitrogen was unaffected, and hydrogen was produced. Also, traces

of methane and carbon dioxide were produced. The ratio of $H_2/CO_2/CH_4$ was nominally 1.0/0.03/0.01. In contrast to concrete radiolysis, hydrogen pressure did not attain an equilibrium up to at least 200 psi, the highest pressure tested. This implies that in sealed canisters of this type of waste, very high hydrogen pressures could be attained. The extent of this hydrogen pressurization is easily calculated from the total radiation dose at any time, the amount of material irradiated, the free volume in the container, and the yield of hydrogen in terms of molecules produced per 100 eV of energy absorbed (G value).

Experiments varying the organic/vermiculite ratio indicated (SLIDE 11) that hydrogen resulted only from the energy sorbed by the organic material and not from that sorbed by the vermiculite. This indicates that energy is not transferred between the organic material and the vermiculite. For calculating hydrogen pressure, values for $G(H_2)$ are obtained from extrapolation of the data in SLIDE 11 to 100% organic material. The total energy absorbed by the waste form then has to be multiplied by the mass fraction of organic material present. There is a slight dependence of these values on dose rate; and at the low dose rates of the nuclear wastes, the values are 4.5 molecules/100 eV for octane, and 2.0 molecules/100 eV for oil. The value of $G(H_2)$ for octane is equal to that for radiolysis of the pure liquid, further indicating that vermiculite is not transferring energy with the octane. Pressurization from alpha-radiolysis is shown in SLIDE 12. Again,

hydrogen and traces of carbon dioxide and methane were produced, and oxygen was consumed.

Values for $G(H_2)$ based on energy sorbed by the organic were 4.3 for octane and 2.7 for the oil. These are close to the values for gamma-radiolysis and indicate only a slight effect of the LET of the radiation. This small effect of LET has been observed in radiolysis of many organic compounds.⁴

These results with organic wastes indicate that at least 200 psi of hydrogen will be produced during long term storage.

CELLULOSIC MATERIALS

One rather abundant form of nuclear waste is absorbent cellulosic material (laboratory tissues, "atomic wipes," etc.) contaminated with alpha-emitting isotopes. This material is retrievably stored at SRP in sealed 55-gallon drums. Results of radiolytic gas production from ^{244}Cm alpha-radiolysis of cellulosic tissues are presented in SLIDE 13. This slide shows the increase in gas volume at atmospheric pressure and ambient temperature. Oxygen was consumed, nitrogen was unaffected, and hydrogen, carbon dioxide, and carbon monoxide were produced at relative rates of 1.0/0.7/0.3, respectively.

The 100-eV yields for gas production were calculated from the slopes of the lines, the ideal gas law, and the dose rate to the tissues calculated from the amount of ^{244}Cm present. SLIDE 14 shows that these yields decrease with increasing total dose to the cellulose. This probably results from formation of products

that produce less gas as radiation progresses. Data in SLIDE 14 also indicate that the 100-eV yields are independent of dose rate (i.e., at any dose rate, the same number of gaseous molecules are produced per 100 eV of energy absorbed). SLIDE 15 shows the physical damage to the cellulose.

As with the octane and oil, hydrogen pressures can be estimated by knowing the amount of activity present, the gas volume, and the value for $G(H_2)$. Although experiments at high pressures were not performed, the rate of hydrogen pressurization is probably independent of the hydrogen pressure, as it was with octane and pump oil. On this basis, large amounts of hydrogen may accumulate during storage of this type of waste.

SUMMARY

The above experiments have indicated that hydrogen will be produced during storage of radioactive wastes containing water or organic material. With water, hydrogen will reach a low equilibrium pressure during the first 200 years storage, but after several centuries will increase to high pressures from alpha-radiolysis. With organic material, hydrogen pressurization will increase linearly to high pressures. Currently, the amount of hydrogen produced in a waste container is being held to low pressures by limiting the amount of radioactivity stored in that container. Hydrogen generation can be eliminated completely by storing the waste in absence of water or organic material. One method being evaluated is to calcine the fission product sludges and incorporate

them in glass. For organic waste, a method being evaluated is to incinerate the material and incorporate the ash in glass.

REFERENCES

1. J. A. Stone. *Evaluation of Concrete as a Matrix for Solidification of Savannah River Plant Waste*. USERDA Report DP-1448, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, South Carolina (1976).
2. I. G. Draganic' and Z. D. Draganic'. *The Radiation Chemistry of Water*. Academic Press, New York (1971).
3. T. B. Rhinehammer and E. A. Mershad. "Techniques and Facilities for Handling and Packaging Tritiated Liquid Wastes for Burial" in *Proceedings of the 2nd AEC Environmental Protection Conference*, Albuquerque, New Mexico, April 16, 1974. USAEC Report WASH-1332, Vol. 2, pp 1067-1088 (1974).
4. W. G. Burns and R. Barker. "Dose Rate and Linear Energy Transfer Effects in Radiation Chemistry." *Prog. Reaction Kinetics* 3, 305 (1965).

**NOMINAL COMPOSITION
OF WASTE FORMS**

A. High Alumina Cement (wt %)

Al_2O_3 , 41; CaO , 37; SiO_2 , 9; Fe_2O_3 , 6; MgO , 1; Other, 6.

B. Savannah River Plant High Level Radioactive Waste

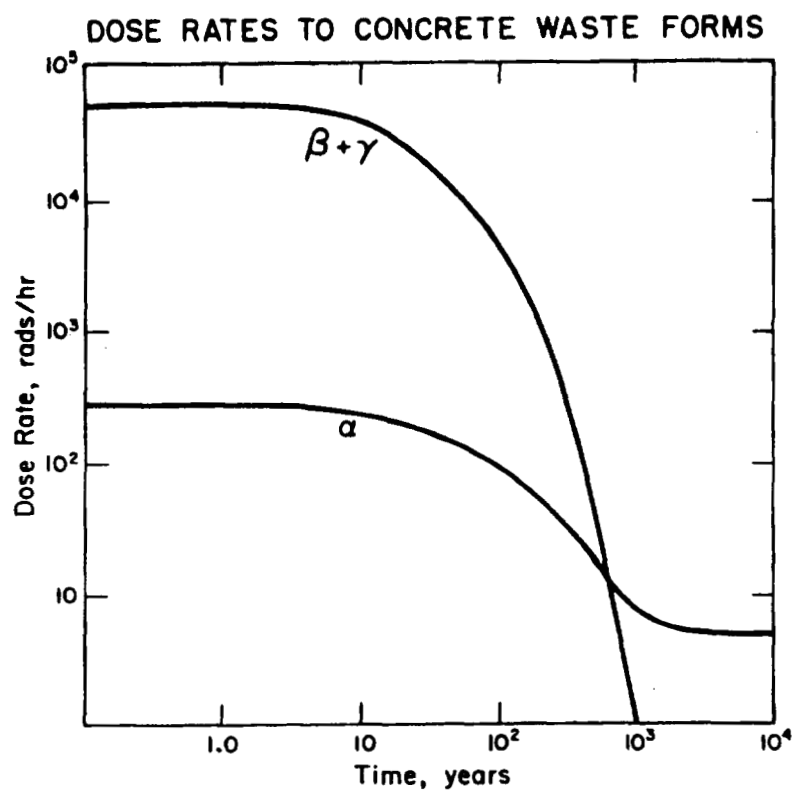
Nonradioactive Ions (wt %)

Fe, 33; Al, 2; Mn, 2; U, 4; Na, 3; Ca, 3; Sr, 3.

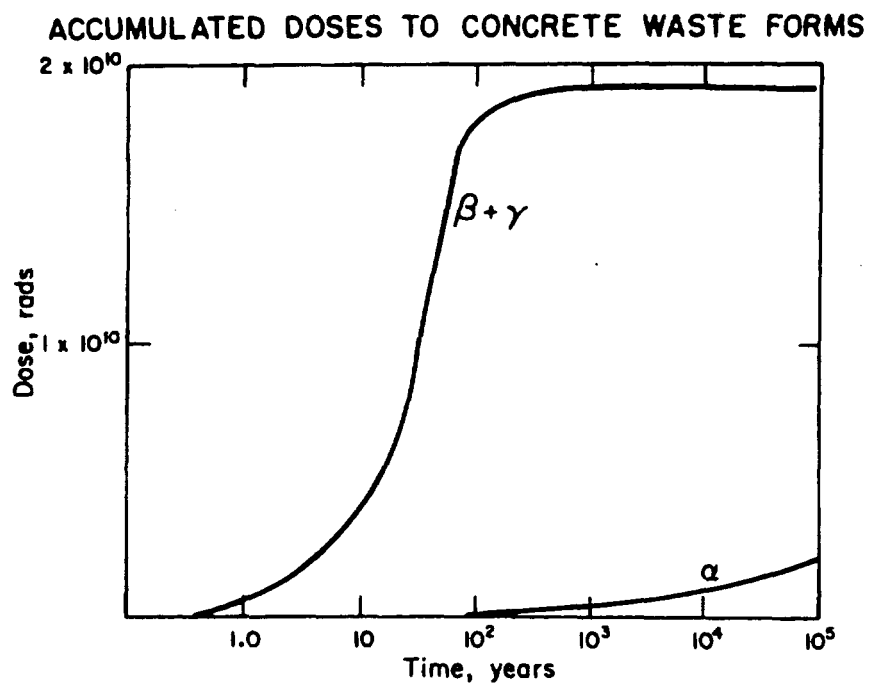
Radioactive Isotopes (mCi/g)

^{90}Sr , 100; ^{137}Cs , 100; ^{144}Ce , 30; ^{106}Ru , 10; ^{154}Eu , 1.

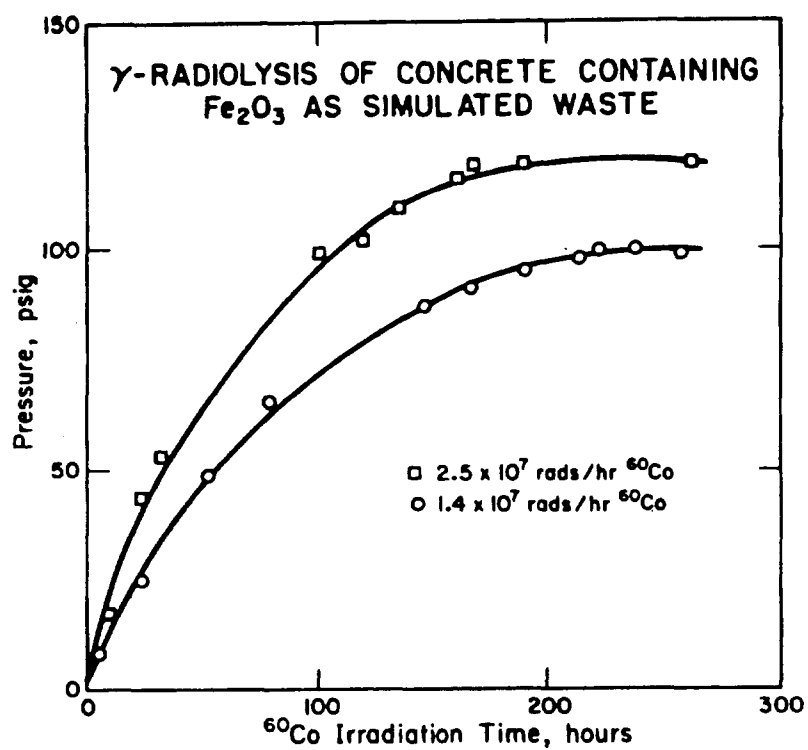
**SLIDE 1. Nominal Composition of High Alumina Cement and
SRP High Level Radioactive Waste**



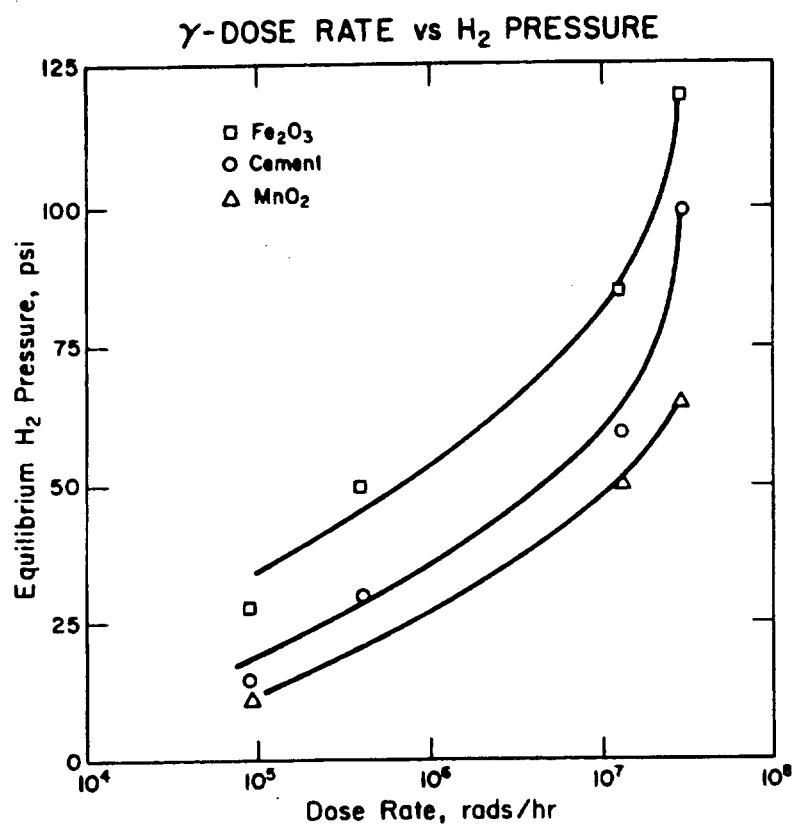
SLIDE 2. Dose Rates to Concrete Waste Forms
Containing SRP Waste



SLIDE 3. Accumulated Doses to Concrete Waste Forms Containing SRP Waste



SLIDE 4. High Dose Rate ^{60}Co Gamma-Radiolysis of Concrete and Fe_2O_3 as Simulated Waste



SLIDE 5. Effect of Dose Rate on H₂ Equilibrium Pressures

7

EVALUATION OF CONCRETE AS A MATRIX FOR SOLIDIFICATION OF SAVANNAH RIVER PLANT WASTE

by

J. A. Stone

Approved by

M. L. Hyder, Research Manager
Separations Chemistry Division

Publication Date: June 1977

see p. 45 →

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PREPARED FOR THE U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION UNDER CONTRACT AT(07-21-1

ABSTRACT

The properties of concrete as a matrix for solidification of Savannah River Plant (SRP) high-level radioactive wastes were studied. In an experimental, laboratory-scale program, concrete specimens were prepared and evaluated with both simulated and actual SRP waste sludges. Properties of concrete were found adequate for fixation of SRP wastes. Procedures were developed for preparation of simulated sludges and concrete-sludge castings. Effects of cement type, simulated sludge type, sludge loading, and water content on concrete formulations were tested in a factorial experiment. Compressive strength, leachability of strontium and plutonium, thermal stability, and radiation stability were measured for each formulation. From these studies, high alumina cement and a portland-pozzolanic cement were selected for additional tests. Incorporation of cesium-loaded zeolite into cement-sludge mixtures had no adverse effects on mechanical or chemical properties of waste forms. Effects of heating concrete-sludge castings were investigated; thermal conductivity and DTA-TGA-EGA data are reported. Formulations of actual SRP waste sludges in concrete were prepared and tested for compressive strength; for leachability of ^{90}Sr , ^{137}Cs , and alpha emitters; and for long-term thermal stability. The radioactive sludges were generally similar in behavior to simulated sludges in concrete.

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Typical weight losses on heating were 6 to 14% in the first month, then an additional 1 to 2% loss in the next two months. Largest weight losses were with Sludge I specimens, which also required the largest amounts of water in the formulations. Smallest weight losses were with Sludge II specimens, even though about the same amount of water was required in Sludge II and III formulations; the small weight loss suggests that negligible mercury was lost by decomposition of HgO . Specimens made with high-alumina cement also had significantly smaller weight losses than specimens made with portland cements.

Radiation Stability

A concrete-sludge casting from each formulation was gamma-irradiated to 10^{10} rads, to simulate the total radiation dose expected from self-irradiation by SRP waste over a 100-year storage period. During irradiation, the samples were heated to temperatures up to 95°C by gamma ray absorption. Compressive strength measurements after gamma irradiation gave results that were not significantly different from those for samples exposed only to heat (in thermal stability tests discussed in the previous section). Although the effects of radiation and heat were intermingled, no evidence was found for any effect of radiation on the strength of concrete-sludge specimens.

As a final check on strontium leachability under conditions of high sludge content, heat, and gamma radiation, a small factorial experiment was performed with only sludge type and cement type as factors. Specimens with 40% sludge content and ideal water content were gamma-irradiated and then measured for strontium leachability. In every case, the strontium leachability after six-weeks leaching was markedly lower for irradiated than for unirradiated specimens by factors ranging from 2 to 20. The largest reduction in leachability was exhibited by specimens containing Sludge I, as shown in Figure 8. Again, no adverse effects could be ascribed to radiation.

Experimental Procedure. Castings were gamma-irradiated in a ^{60}Co facility at a dose rate of 3.5×10^7 rads/hr. Figure 9 shows concrete-sludge castings in an irradiation rack designed to hold 76 pieces. The sample-loaded rack was sealed in a special vessel, shown in Figure 10, for placement inside the irradiation facility. Three separate irradiations were made, each about 300 hr for total dose of 10^{10} rads. Because the irradiation facility was not continuously available, each irradiation required about three weeks. With forced-air cooling, the irradiation temperatures were 65 to 95°C . One casting from each of 168 formulations was irradiated for compressive strength

tests. An additional casting of 24 formulations (6 with no sludge and 6 with each simulated sludge at 40% loading) was irradiated for subsequent measurements of strontium leachability. Experimental methods for both tests were the same as described previously.

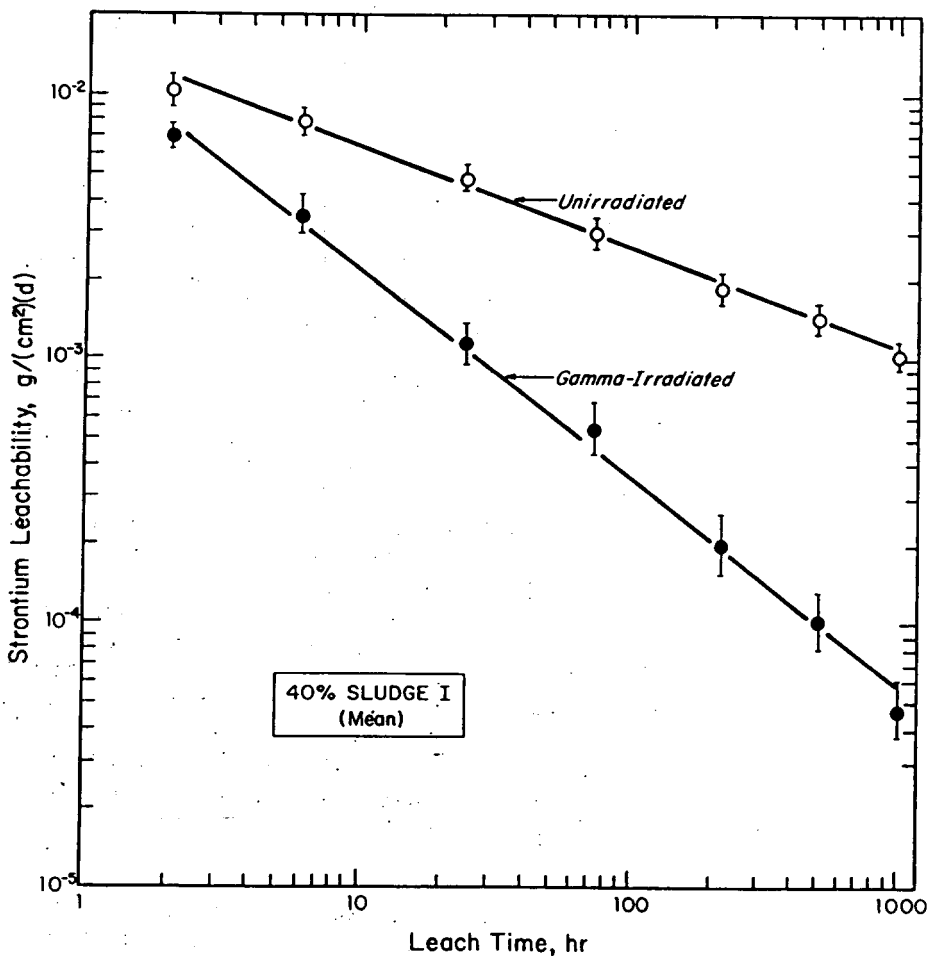


FIGURE 8. Effect of Gamma Irradiation on Strontium Leachability

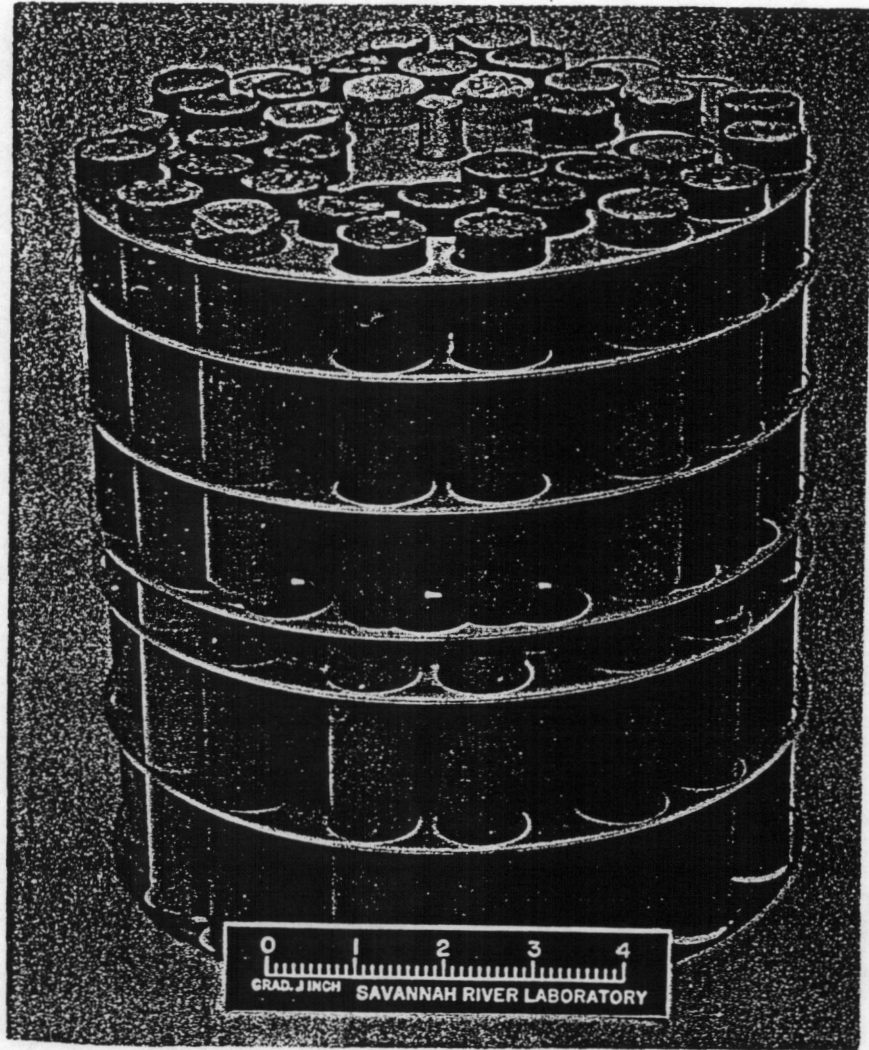


FIGURE 9. Irradiation Rack for Concrete-Sludge Castings

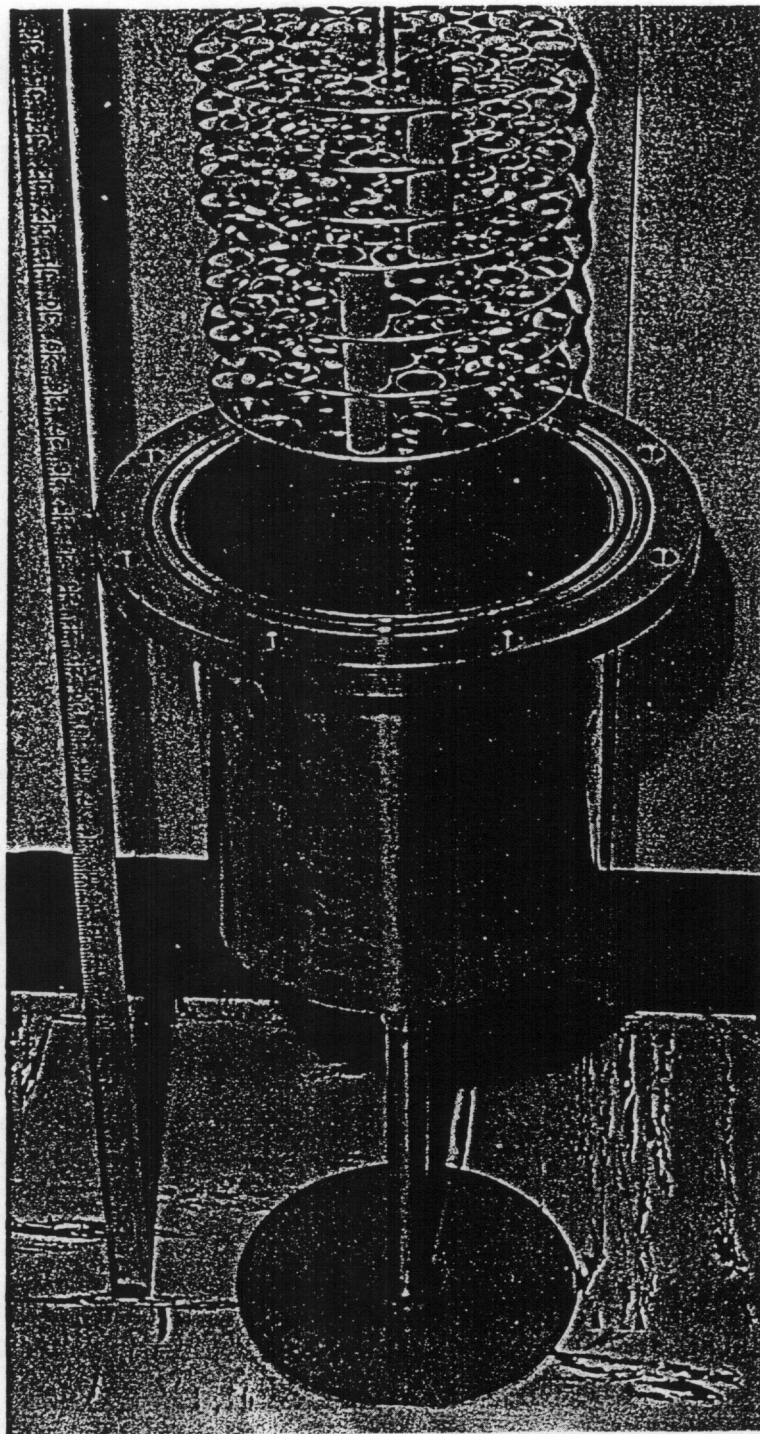


FIGURE 10. Vessel for Gamma Irradiations

Results. The compressive strength data were treated statistically with an analysis of variance for each sludge type separately. Each statistical analysis was for a 6 x 3 x 3 factorial experiment with duplicate samples, the factors being cement type, sludge content, and water content. The principal features of compressive strength behavior of concrete-sludge specimens again were found with the gamma-irradiated specimens: sludge content was of predominant significance, cement type was less significant, and water content was not statistically significant. The data were averaged over water contents and duplicate specimens to give compressive strengths that are the average of six data points.

The compressive strengths of irradiated and unirradiated specimens are compared in Table 14, which gives the percent difference in strength after irradiation. Changes less than about 20% were not statistically significant. The data are very similar to those for thermal stability (Tables 11 and 12), even though the experimental conditions were quite different. Most of the compressive strengths for gamma-irradiated specimens were not statistically different from those of specimens heated for thermal stability tests. Exceptions are for specimens containing 40% Sludge II and specimens containing Type I-P cement, all of which are significantly stronger than the heated samples. Because the irradiated specimens also were heated, the effects of radiation and heat are intermingled. Many of the reductions in strength can be attributed to heat alone, but none to radiation alone.

Strontium leachabilities of other irradiated specimens were measured.

Specimens of castings irradiated for strontium leachability tests formed a 6 x 3 factorial experiment with duplicate samples. The factors were the six cement types and the three sludge types, each combination having 40% sludge content and ideal water content. In addition, specimens with each cement type and no sludge were irradiated and leached. As before, the strontium leach tests were performed at seven time periods, from 2 to 1008 hours. An analysis of variance was made for each time period separately. The effect of sludge type was highly significant at all time periods. The effect of cement type was not statistically significant, except for the first and last time periods. The data were averaged over cement types and duplicate specimens to give strontium leachabilities that are the average of 12 data points.

TABLE 14

Radiation Stability of Concrete Waste Forms Gamma
Irradiated to 10^{10} rads

<i>Sludge Type Content, %</i>		<i>% Change^a in Compressive Strength, for Cement Types</i>						
		<i>I</i>	<i>II</i>	<i>III</i>	<i>V</i>	<i>I-P</i>	<i>HAC</i>	<i>Mean^b</i>
None	0	- 12	+ 3	-10	-16	+10	+ 3	- 4
I	10	<u>- 27</u>	<u>-20</u>	<u>-28</u>	<u>-29</u>	- 6	<u>-20</u>	<u>-22</u>
	25	- 17	- 6	<u>-34</u>	-11	+ 1	+ 2	<u>-12</u>
	40	<u>+134</u>	-17	+ 9	- 7	-17	-15	+ 6
II	10	<u>- 23</u>	<u>-38</u>	-12	<u>-23</u>	+ 9	<u>-28</u>	<u>-20</u>
	25	- 14	-15	+ 4	-15	+ 4	<u>-23</u>	<u>-10</u>
	40	+ 3	+21	+ 7	+ 3	+11	-13	+ 5
III	10	<u>- 34</u>	- 9	<u>-23</u>	<u>-23</u>	-12	+ 4	<u>-17</u>
	25	<u>- 25</u>	<u>-19</u>	<u>-35</u>	- 6	+ 3	- 7	<u>-16</u>
	40	<u>- 19</u>	-13	<u>-25</u>	+ 1	- 7	<u>+19</u>	<u>- 8</u>

a. Underlined values are statistically significant differences between irradiated and unirradiated specimens.

b. Geometric mean.

Table 15 shows the time behavior of strontium leachability for each sludge type. These data also are compared with similarly averaged values for unirradiated specimens as percent differences in leachability after irradiation. Changes less than about 30% were not statistically significant. Strontium leachability of the irradiated specimens also decreased monotonically with time, as shown in Figure 8. For every sludge type, the strontium leachability was generally lower for the irradiated than for the unirradiated specimens. The differences were particularly striking after 1008-hr leaching; the leachability for Sludge I specimens was lower by a factor of ~ 20 (Figure 8), and was lower for Sludge III specimens which approach 1×10^{-5} g/(cm²)(d). For irradiated specimens the strontium leachability decreased in the order

Sludge II > Sludge I > Sludge III

For 40% sludge content, this ordering reverses the positions of Sludges I and II from that for unirradiated specimens.

Neither the strontium leachability nor the compressive strength measurements showed large differences among the cement

types for irradiated specimens. In the leach tests, no significant differences were found, except at 2 hr and at 1008 hr. In both cases, the strontium leachabilities of HAC specimens did not decrease as much as those of portland cement specimens. At these two times, the average value for HAC was about a factor of two larger than those for the other cements. At 40% sludge content, the compressive strengths of HAC specimens were significantly larger than those of the other cements, with average values of 3723, 5095, and 4003 psi for Sludges I, II, and III, respectively. The corresponding values for Type I-P cement specimens were 1983, 3684, and 2868 psi.

TABLE 15

Strontium Leachability of Selected Concrete Waste Forms
Gamma Irradiated to 10^{10} rads

Time, hr	<i>Sr Leachability, ^{a,b,c} 10^{-3} g/(cm²)(d), and % Change, for Sludge Types</i>							
	No Sludge		40% Sludge I		40% Sludge II		40% Sludge III	
2	7.7	(+48%)	7.1	(-33%)	6.5	(-12%)	2.8	(+ 4%)
6	4.2	(-10%)	3.6	(-56%)	4.4	(-15%)	1.6	(+ 2%)
24	2.3	(-14%)	1.2	(-77%)	1.8	(-42%)	0.43	(-34%)
72	1.3	(-11%)	0.55	(-82%)	1.4	(-25%)	0.17	(-59%)
216	0.47	(-43%)	0.20	(-89%)	0.65	(-27%)	0.047	(-69%)
504	0.32	(- 9%)	0.10	(-93%)	0.41	(-36%)	0.022	(-76%)
1008	0.092	(-53%)	0.048	(-95%)	0.28	(-62%)	0.011	(-84%)

- a.* % change given in parentheses; underlined values are statistically significant differences between irradiated and unirradiated specimens.
- b.* Each leachability value is the average of 12 data points.
- c.* Error factors ϵ (95% confidence) range from 1.10 to 1.30.

Selection of Optimum Cement Types

The principal conclusions with regard to cement selection are:

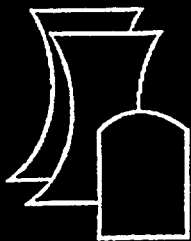
- High-alumina cement was superior to all the portland cements.
- Type I-P cement was slightly better than other portland cements.

On the basis of the compressive strength and strontium leachability tests, HAC was clearly superior. In the thermal and radiation stability tests, HAC specimens underwent larger changes than portland cements but still had as good or better properties. The portland cements were quite similar to each other in all properties measured, and all were poorer than HAC. Of the portland cements, Type I-P had the best all-around properties, especially at 40% sludge content.

In further studies with concrete-sludge waste forms, only HAC and Type I-P cement were used. The portland-pozzolan cement was carried into the next phase of the evaluation in case any severely undesirable property were found later for HAC. With simulated sludges, HAC and Type I-P cement formulations were used to investigate the effects of adding cesium-loaded zeolite and of heating concrete-sludge beyond 100°C. These studies are described in the following sections. Finally, HAC and Type I-P cement were used in formulations with actual SRP waste sludges, described in the latter portion of this report (page 71).

Effects of Adding Cesium-Loaded Zeolite

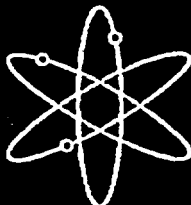
Two series of concrete formulations were prepared containing cesium-loaded zeolite that was tagged with ^{137}Cs tracer. One of the series contained simulated sludges at 40% sludge content but with 1/16 of the sludge replaced by cesium-loaded zeolite. This mixture has been proposed as a means of locally distributing the heat from decay of SRP ^{137}Cs waste among concrete waste forms. The other series contained cesium-loaded zeolite to 40%, but with no sludge. The formulations were measured for their compressive strengths. Specimens with only cesium-loaded zeolite had a compressive strength with the sludge-zeolite mixture. For HAC and 40% cesium-loaded zeolite had a compressive strength and $\sim 10^{-5}$ g/(cm²) (d) cesium leaching; the corresponding values for the 2.5% zeolite were $\sim 3,000$ psi and $\sim 10^{-5}$ g/(cm²) (d).



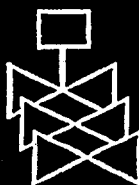
Hydrogen Generation in TRU Waste Transportation Packages



Lawrence Livermore National Laboratory



U.S. Nuclear Regulatory Commission
Office of Nuclear Material Safety and Safeguards
Washington, DC 20555-0001



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Manuscript Completed: February 2000
Date Published: May 2000

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EXECUTIVE SUMMARY

An analysis of hydrogen generation in transportation packages for transuranic (TRU) waste materials is necessary to ensure that the packages do not accumulate an unsafe concentration of hydrogen (or other flammable) gas. As a result of safety considerations related to flammability, the concentration of hydrogen in the transportation package is limited to a level below the lower flammability limit. (Appendix E gives the lower flammability limit for common gases and vapors.) Mechanisms for hydrogen generation in transportation packages include (1) chemical reaction, (2) thermal degradation, (3) biological activity, and (4) radiolysis. The focus of this report is on radiolytic hydrogen generation, with general information provided on hydrogen generation via chemical reaction, thermal degradation, and biological activity.

Chemical reactions are capable of producing large quantities of hydrogen, but the contents of TRU waste transportation packages are typically controlled to limit any reaction among the contents or reactions between the contents and the packaging that would produce significant quantities of hydrogen or other gases. If chemical reactions that generate hydrogen (or other flammable gases) are expected to occur in the TRU waste transportation package, these gas sources should be included in an analysis of the flammable gas levels and pressures in the containment vessel(s) and related confinement barriers. Examples of chemical reactions that generate hydrogen are listed in Appendix A.

Thermal degradation of packaging materials or content constituents can be a source of flammable gaseous species if the temperature of the material is above its maximum continuous service temperature. Species released due to thermal degradation of organic materials are typically carbon dioxide, carbon monoxide, and small amounts of low molecular weight flammable species, but usually do not include significant amounts of hydrogen gas. For TRU wastes at temperatures up to 250°F, no significant thermal degradation is expected to occur in most materials, however, some out-gassing is expected from materials that have a maximum continuous service temperature below 250°F. These materials include nylon, polyethylene, polystyrene, polyvinylchloride, and epoxy. The species released from these materials at temperatures up to 250°F include solvents, plasticizers, and other low molecular weight flammable materials. Although the gases released from thermal degradation of materials below 250°F are not expected to include significant hydrogen or other flammable species, the gases that are determined to be released should be included in an analysis of the flammable gas levels and the pressures in the containment vessel(s) and the related confinement barriers. A general discussion concerning thermal degradation is presented in Appendix B.

Biological generation of hydrogen (or other gas) requires biologically contaminated waste and the nutrients and conditions conducive to biological growth within the transportation package. The nutrient and environmental conditions in TRU waste transportation packages are typically not sufficient to sustain biological growth. However, when chemical reactions are expected to occur, thermal degradation of materials is expected to occur, or it is suspected that the TRU waste has biological contamination, tests may need to be performed to estimate the expected hydrogen generation under normal and hypothetical accident transportation conditions. A general discussion of biologically generated gases in TRU waste transportation packages is in Appendix C.

Radiolytic generation of hydrogen occurs when ionizing radiation (e.g., α , β , or γ) interacts with hydrogenous materials. The metric for hydrogen generation from a particular material undergoing radiolysis is the G-value, which has units of molecules of gaseous hydrogen product per 100 eV of radioactive decay energy absorbed. Appendix D provides information concerning G-values for various hydrogenous materials commonly present in TRU waste. This report defines waste types according to

P	gas pressure [atm]
P_0	pressure when container was sealed [atm]
P_1	gas pressure at position "1" [atm]
P_2	gas pressure at position "2" [atm]
P_a	average pressure [atm]
P_d	downstream pressure [atm]
P_F	fraction of particles that reach plastic packaging material
P_P	permeability [mole-cm/s-cm ² -mmHg]
P_{ss}	steady-state pressure [atm]
P_u	container pressure or upstream pressure [atm]
$P_{u,0}$	container pressure or upstream pressure at time=0 [atm]
Q	volumetric rate of radiolytically-generated gas [cm ³ /s]
t	time [seconds]
t_c	thickness of confinement barrier [cm]
t_R	range of particles in material [cm]
$t_{5\%}$	time to reach 5 volume percent hydrogen [s]
T	gas temperature [K]
T_0	temperature when container was sealed [K]
T_1	effective hydrogen transport rate through barrier #1 [mole H ₂ /s-mole fraction]
T_2	effective hydrogen transport rate through barrier #2 [mole H ₂ /s-mole fraction]
T_3	effective hydrogen transport rate through barrier #3 [mole H ₂ /s-mole fraction]
T_D	hydrogen transport rate [mole H ₂ /s-mole fraction]
T_{eff}	effective hydrogen transport rate [mole H ₂ /s-mole fraction]
r	radius of cylinder [cm]
R	gas law constant [82.05 atm-cm ³ /gmol-K]
R_M	molar hydrogen generation rate [gmol H ₂ /s]
V	container void volume [cm ³]
$x_{H_2,in}$	hydrogen mole fraction inside the confinement barrier
$x_{H_2,out}$	hydrogen mole fraction outside the confinement barrier

HYDROGEN GENERATION IN TRU WASTE TRANSPORTATION PACKAGES

1. INTRODUCTION

1.1 Background

Packages for transporting certain quantities and types of radioactive material are designed and constructed to meet the requirements of Title 10, Code of Federal Regulations, Part 71 (10 CFR Part 71). An evaluation that demonstrates compliance with this regulation is submitted to the U.S. Nuclear Regulatory Commission (NRC) in the application for package approval.

One concern in the evaluation of packages to transport transuranic (TRU) waste is the production of hydrogen and other flammable gases. Regulations in 10 CFR 71.43(d) specify that no significant chemical, galvanic, or other reaction may occur among packaging components, among package contents, or between the packaging and the package contents. The effects of radiation must also be considered.

For the purposes of this report, TRU waste is considered to be radioactive waste that (1) is subject to the requirements of 10 CFR Part 71, (2) contains nuclides with an atomic number greater than 92, and (3) is not considered high-level waste, as defined by 10 CFR 60.2. Other documents (U.S. EPA, 40 CFR Part 191; DOE Order 5820.2A) have specified alternative definitions, including limits on half-life and specific activity, which are not significant for transportation evaluations. The majority of radionuclides in TRU waste decay by alpha (and gamma) emission, but some nuclides (and their progeny) are beta or beta-gamma emitters.

TRU waste usually consists of transuranic nuclides mixed with plastics, metal, glass, paper, salts, absorbents, oxides, filters, filter media, cloth, concrete and other waste materials. Typical waste includes contaminated clothing, paper, tools, and similar items. Most TRU waste exists in solid form, but liquids and sludges are also encountered. Some liquids are solidified, and some sludges dewatered, prior to transport.

1.2 Purpose and Scope

The purpose of this report is to provide information on the production of hydrogen and other flammable gases in transportation packages for TRU waste. Section 2 discusses the various mechanisms of gas production and provides general guidelines for assessing their importance. Radiolysis is usually the most significant mechanism for gas generation in TRU waste. Section 3 discusses radiolysis in detail and provides information on generation rates in various organic and inorganic wastes. Based on these rates, Section 4 discusses the calculation of gas concentration as a function of time and decay heat for various TRU contents and packaging configurations in order to determine the time at which the flammability limit is reached. Section 5 presents information concerning the control of hydrogen gas generation. An extensive list of references is presented in Section 7.

Because hydrogen is the most significant flammable gas produced in TRU waste transportation packages, this report focuses primarily on the generation of hydrogen. Situations in which other flammable gases should be considered, however, are noted as appropriate.

This report provides information that may be used by NRC staff to evaluate the potential for hydrogen generation in transportation packages, and describes an acceptable method to demonstrate that flammable concentrations of hydrogen will not occur within packages during transport. Control of hydrogen in

2. MECHANISMS FOR HYDROGEN GENERATION

Mechanisms for hydrogen gas generation in transuranic waste transportation packages include (1) chemical reactions, (2) thermal degradation, (3) biological activity, and (4) radiolysis. In general, hydrogen generated by chemical reactions in transportation packages can be avoided. Thermal effects generate significant amounts of flammable gases only if polymers or other organics within the package undergo thermal degradation. Biological generation of gases occurs only if the contents are sufficiently contaminated before loading and the contents have sufficient substrate to support biological growth. This section briefly discusses the first three mechanisms and their potential contribution to the total hydrogen generation rate in a transportation package. Radiolysis, which is generally the most important mechanism for hydrogen (and flammable gas) generation, is introduced in this section and discussed in detail in Section 3.

2.1 Chemical Reactions

For TRU wastes that are dewatered, solidified, or concreted, the hydrogen production due to chemical reaction should be minimal as long as the content constituents and materials of packaging are chosen so that there will be no significant chemical, galvanic, or other reaction among the packaging components, among the package contents, or between the packaging components and the package contents (10 CFR 71.43(d)). For contents that include water, organic materials (e.g., sludges), or mixtures of potentially reactive species, the rate of hydrogen generation from chemical reaction should be determined and the related consequences analyzed in the safety evaluation of the transportation package. Appendix A provides a summary of some common types of chemical reactions that can lead to hydrogen generation.

2.2 Thermal Degradation

Thermal degradation of organic materials in TRU waste transportation packages is usually not a significant source of hydrogen or other flammable gas generation for waste temperatures below ~250°F. The major constituents released when an organic material undergoes thermal degradation are carbon dioxide and carbon monoxide, and small amounts of low molecular-weight flammable species. Therefore, gases generated due to thermal degradation can contribute to the total pressure but typically do not contribute significantly to the inventory of flammable species in the containment vessel. For TRU wastes that are above 250°F, tests may be needed to determine the amount of gas, both flammable and nonflammable, which will be released during transportation.

Although TRU waste contents at lower temperatures are not expected to have significant thermal degradation, some small amounts of off-gassing can occur for materials that have maximum continuous service temperatures below 250°F (e.g., nylon, polyethylene, polystyrene, polyvinylchloride, and epoxy). The constituents of this off-gassing can be released solvents, plasticizers, and other low molecular weight flammable materials. Neither off-gassing nor thermal degradation of organic materials releases significant quantities of hydrogen gas. Although TRU waste materials below about 250°F are not expected to release significant quantities of flammable materials, it is important to estimate the rate of accumulation of these materials in the containment vessel (along with the rate due to other mechanisms, including hydrogen generation during storage before transportation) to verify that a flammable mixture will not be formed during transportation.

Appendix B provides general information the thermal degradation of TRU wastes (including the maximum continuous service temperature and results from thermal degradation experiments for various plastics).

high-energy gamma and low-atomic-number materials, the gamma is scattered with a reduced energy. Compton interactions in water predominant from approximately 30 keV to 20 MeV.

Radiolytic G-Values

Regardless of the type of ionizing radiation causing the radiolysis, the measure of radiolytic gas generation is the G value. G values have units of number of gas molecules produced per 100 eV of radiation energy absorbed. Factors affecting radiolytic gas generation from the interaction of alpha, beta or gamma radiation with matter include: (1) the linear energy transfer (LET), (2) the irradiation environment (e.g., pressure, temperature, pH, and gases present), (3) the absorbed dose, (4) the dose rate, (5) the material composition, (6) the range of the incident radiation, (7) the configuration of the radioactive material relative to the material undergoing radiolysis, and (8) energy transfer considerations. Radiolytic G-values for various materials are discussed in detail later in this report and in Appendix D.

2.4.1 Linear Energy Transfer Effect

Differences in G values for a material irradiated by different types of radiation are ascribed to the way in which energy is lost in matter. Linear energy transfer (LET) is the energy loss per unit length of an ionizing particle traveling through a material. An average LET is calculated by dividing the initial energy of a particle by its range in the material.

Although differences in radiolysis products have been found for materials subject to different types of radiation, these differences are relatively small, and for the purposes of this document, bounding radiolytic G values are presented to enable bounding estimates of the flammable gas generation rates. Typically, alpha-radiolysis of a material will yield the bounding G values for gas generation.

2.4.2 Temperature

Most chemical reaction rates depend on temperature. The rate constant, k , can be described using the Arrhenius law: $k = A \exp(-E_a/RT)$, where E_a is the activation energy, A is the pre-exponential factor, R is the gas law constant, and T is the absolute temperature. The activation energy is the energy necessary to initiate the reaction.

The activation energy for radiolytic gas generation in most materials appears to be less than or equal to 3 kcal/gmol, which results in a weak temperature dependence (NRC Docket No. 71-9218, Aug. 11, 1999). E_a for polyvinylchloride (PVC) is ~3 kcal/gmol, and E_a for polyethylene is about 0.8 kcal/gmol. Alpha radiolysis data for cellulose indicate that the E_a for radiolysis is about 1-2 kcal/gmol (Kosiewicz 1981; Zerwech 1979). The temperature dependence of $G(H_2)$, which is the radiolytic G value for hydrogen generation, in liquid n-hexane and neopentane corresponds to an activation energy of ~3 kcal/gmol (Bolt and Carroll 1963). The radiolysis of water has been found to be temperature-independent, and therefore has an apparent activation energy of 0 kcal/gmol.

The relationship between the rate constants k_1 and k_2 at two different temperatures T_1 and T_2 is given by:

$$\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{E_a}{R}\right) \left(\frac{T_2 - T_1}{T_2 T_1}\right). \quad 2.1$$

The G-value at a temperature T_2 can be calculated from a known G-value at a temperature T_1 :

conservatism in the results, G values are often expressed as initial G values or as the G values extrapolated to near zero absorbed dose.

2.4.6 Dose Rate

In a number of experiments, the G values for specific materials were independent of dose rate for the dose rate ranges studied (e.g., Bibler 1976; Chapiro 1962). Others (O'Donnell and Sangster 1970), however, others have found that G values may exhibit a non-linear dependence on dose rate. These observed non-linearities may be due to radiation-initiated chain reactions.

Some apparent dose rate effects may be caused by an increase in the material's temperature. Since the major portion of the absorbed radiation energy is converted to heat, at high dose rates the temperature of the material could rise significantly. At high localized temperatures, reaction pathways different from those occurring at low dose rates may dominate (Schnabel 1981).

Physical dose-rate effects have been observed for numerous materials subject to gamma radiation. Most of these experiments were performed in oxygen-containing environments in an effort to simulate accelerated aging. Physical dose rate effects depended on material type, aging conditions, sample geometry, and the degradation parameter being monitored. In general, more degradation was produced for a given total dose as the dose rate was lowered. Diffusion-limited oxidation processes were shown to be the cause of such effects. When the oxidation processes in a material consume dissolved oxygen faster than it can be replenished from the atmosphere surrounding the material (from diffusion), a heavily oxidized layer of material is formed near the sample surface, and oxygen depletion may occur in the sample interior. As the dose rate is reduced, however, oxidation of the sample interior increases due to the longer times available for the diffusion processes.

The dose rate effects leading to sample oxidation depend on the range of the radiation. For alpha radiation, the reaction will be dose-rate independent if the oxygen can easily diffuse to a depth equal to the range of the alpha particles. Likewise, the physical dose-rate effects can be minimized in gamma radiolysis experiments by using thin film samples (Bonzon 1986).

Chemical dose-rate effects involving the interactions between radiation and thermal degradation have been reported for polyethylene and PVC irradiated in the presence of oxygen (Gillen et al. 1982). These experiments showed that the most severe mechanical degradation occurred when radiation was combined with elevated temperature. The reported degradation was much greater than the sum of the damage caused by separate exposure to radiation and to the elevated temperature. This effect was attributed to an oxidation mechanism, in which peroxides initially formed by the radiation were decomposed. The magnitude of these effects could be reduced by removing any oxygen before the irradiated materials were heated.

2.4.7 Specific Material Composition

Many of the radiolysis experiments reported in the literature were performed using pure polymeric materials. However, commercial plastics differ from the pure polymers because they contain large fractions of various additives, such as stabilizers and plasticizers. These additives can significantly influence the amount and species of gases generated by thermal degradation and radiolysis.

Liquid plasticizers are added to polymers such as PVC or cellulose esters to increase flexibility. These compounds typically have low volatility, but may be emitted from the polymer upon heating. Plasticizers in PVC commonly comprise about 30-40% of the total material. Most of the plasticizers are combustible, and lower the flame resistance and softening points of the polymer products (Deanin 1972).

2.4.8.3 Particle Size of the Contaminant

The plutonium contaminants in TRU wastes are typically in particle form as plutonium dioxide or hydroxides, but may sometimes be in the form of plutonium nitrate from solution in nitric acid. If the plutonium is in particle form, some of the alpha particles will interact with the plutonium or oxygen atoms within the particle in the process known as self absorption, rather than with the surrounding waste material. The fraction of alpha particle energy escaping from PuO_2 particles as a function of particle radius and initial energy has been calculated (NRC Docket No. 71-9218, Aug. 11, 1999; VanDevender 1984; Cowell 1984; Ziegler et al. 1985).

Self absorption is most likely the reason behind the observation that the measured $G(\text{H}_2)$ value for ^{238}Pu dissolved in nitric acid is about 2.5 times the $G(\text{H}_2)$ value for 2 μm particles of the oxide (Bibler 1979). Similarly, the gas generation rate obtained from particulate-contaminated waste may be less than the rate predicted using the maximum G values and the total activity of the waste.

Because of uncertainties in measuring particle size distributions of radioactive particles, the uncertainties in ensuring that particle size distributions remain constant when subject to transportation-induced forces, and the marginal benefit of alpha self absorption (only about 20% for 4.5 μm radius particles), self-absorption arguments may be difficult to justify for transportation of TRU waste. As a conservative approach, this document assumes that all alpha energy escapes plutonium particles that have radii less than about 0.5 μm .

2.4.9 Energy Transfer

The energy absorbed at one location on a large molecule may damage a more susceptible site elsewhere on the molecule. This concept of energy transfer from the location where energy is absorbed to the chemical bond that is broken illustrates that the major products of radiolysis are influenced by the molecular structure. Certain structures, such as aromatic rings, seem to absorb ionizing radiation and dissipate it as heat in the form of molecular vibrations and other nondestructive relaxation mechanisms. Systems containing these structures undergo less decomposition than would be expected (O'Donnell and Sangster 1970).

When a homogeneous mixture of two compounds is irradiated, the yields of the different radiolysis products often are directly proportional to the yields from the pure components and their relative proportions in the mixture. This behavior is observed when each component degrades independently of another. However, for some mixtures, energy transfer can occur among the components in the mixture. In a two-component mixture in which one component can transfer energy to the second component, the second component may absorb more energy and be decomposed more rapidly than predicted by its proportion in the mixture.

3. Hydrogen Generation Rates in Transuranic Waste

Table 3.1 Summary of Bounding Radiolytic G Values for Hydrogen and Flammable-Gas Generation

Material	Bounding G(H₂) [H₂ molecules/100 eV]	Bounding G(flame gas) [gas molecules/100 eV]
Water	1.6	1.6
Hydrocarbons:		
Saturated Hydrocarbons	9.0	10.2
Unsaturated Hydrocarbons	3.0	3.0
Aromatic Hydrocarbons	0.6	0.6
Oxygenated Compounds:		
Methanol Gas	10.8	11.1
Alcohols (liquid)	5.4	6.1
Ethers	3.6	3.8
Aldehydes & Ketones	1.5	3.5
Carboxylic Acids	0.8	4.4
Esters	1.0	3.0
Phosphate Esters	2.3	2.4
Halogenated Hydrocarbons:	0.8	0.8
Organic Nitrogen Compounds:	6.35	6.35
Commercial Lubricants:	2.8	2.9
Polymers:		
Saturated Hydrocarbon Polymers	4.0	4.1
Alcohol Polymers	3.5	3.5
Unsaturated Hydrocarbon Polymers	0.7	0.9
Ester Polymers	0.9	1.4
Aromatic Polymers	0.3	0.3
Halogen-Containing Polymers	0.7	0.8
Ion-Exchange Resins	1.7	1.7
Non-Polymer Solids:		
Solidified Aqueous Sludges	0.43 (no experiments)	0.43 (no experiments)
Concretes	0.6	0.6
Absorbed Liquids	depends on liquid and solid	depends on liquid and solid
Solid Organic Acids	2.3	2.6
Asphalt	1.3	1.3
Soil	0.15 (w/ 5% water) 0.37 (w/ $\geq 5.5\%$ water & $\leq 46.4\%$ organic content)	0.15 (w/ 5% water) 0.37 (w/ $\geq 5.5\%$ water & $\leq 46.4\%$ organic content)
Dry, Solid, Inorganics	0	0
Gases:	0	0

3. Hydrogen Generation Rates in Transuranic Waste

liquids having sufficiently low G-values. Cemented organic process solids are included in this waste type.

In this report, the surface-contaminated organic wastes and their organic packaging are assumed to absorb 100% of the available alpha decay energy. The only gas generated by inorganic materials (which are permitted in this waste type) would be oxygen, which would tend to be consumed by oxidation of the plastic packaging materials. Therefore, any inorganic materials present are considered to generate no gas.

Based on experimentally measured G-values, solid organic materials with the following structural groups are acceptable in this waste type: aromatic rings, unsaturated C-C bonds, and C-N triple bonds. Materials for which the G-value at room temperature for flammable gas could be greater than 4.1 are limited to trace quantities (less than 1% by weight). These materials include cellulose nitrate, polyvinyl formate, polyoxymethylene, and poly(olefin sulfones) (based on current data). Other polymers containing ether functional groups may also have high G(flammable gas) values.

Examples of materials acceptable in Solid Organic Waste are listed in Table 3.4.

Table 3.3 Examples of Materials Acceptable in Solid Inorganic Wastes

Asbestos	Grit	Nitrates
Ash	Inorganic filter media	Portland cement
Clays	Inorganic insulation	Salts
Concrete (surface-contaminated only)	Inorganic resins	Sand
Firebrick	Metals	Slag
Fluorco	Metallic oxides	Soil
Glass	Molds & crucibles (e.g., ceramic, graphite)	Soot

Table 3.4 Examples of Material Acceptable in Solid Organic Waste

Aniline-formaldehyde	Phenol-formaldehyde	Polystyrene
Any solid inorganic material	Phenolic resin	Polysulfone
Asphalt	Polyamide	Polytetrafluoroethylene
Bakelite	Polybutadiene	Polyurethane
Cellulose	Polycarbonate	Polyvinyl acetate
Cellulose acetate butyrate	Polychloroprene	Polyvinyl alcohol
Cellulose propionate	Polychlorotrifluoroethylene	Polyvinyl chloride
Cellulose acetate	Polyester	Polyvinylidene chloride
Chlorinated polyether	Polyethylene	Rubber
Chlorosulfonated polyethylene	Polyethylene glycol	Rubber hydrochloride
Detergent (solid)	Polyimide	Sand
Melamine-formaldehyde	Polyisobutylene	Soil
Oil	Polyisoprene	Tributyl phosphate
Organic acids (solid)	Polymethyl methacrylate	Urea-formaldehyde

3. Hydrogen Generation Rates in Transuranic Waste

3.3.1.1 Fraction of Decay Energy Available for Radiolysis—Range of Radiation

The fraction of decay energy available for radiolysis depends on the range of the radiation, the sizes of the radioactive particles, the density of the waste, and the waste configuration.

The fraction of alpha energy emerging from radioactive particles, $F_{P,\alpha}$, depends on the size of the particles. For alpha irradiation, the absorbed dose for waste materials is applicable only to the mass of the waste within the range of the alpha particles. Although plutonium oxalate calcined at 1000°C has been shown to have a particle size distribution such that a maximum of 82% of the alpha radiation energy escapes the particles as a result of self-absorption (NRC Docket No. 71-9218, Aug. 11, 1999), other TRU waste such as HEPA filters may include smaller radioactive particles that exhibit smaller amounts of alpha self-absorption. Since determination of particle size distributions is difficult and particle size distributions may not remain constant under transportation-induced forces, this report conservatively assumes that $F_{P,\alpha}=1=0$. If the particle size distribution of the radioactive particles in the TRU waste is known, and it can be justified that the particle size distribution will not change during loading and transportation, then $F_{P,\alpha}$ may be less than 1.0. The range of alpha particles with energies between 4 and 8 MeV in low density materials can be estimated by the following equation (Liverhant 1960):

$$\text{Range}_\alpha (\text{cm}) = [(1.24 * \text{Particle Energy (MeV)}) - 2.62] \left(\frac{1.2 \times 10^{-3} \text{ g/cm}^3}{\text{Density}} \right) \quad 3.6$$

For a density of plastics and paper of approximately 1 g/cm³, the range of a 5.14 MeV alpha particle (²³⁹Pu) is 4.6x10⁻³ cm, and the range of a 5.59 MeV alpha particle (²³⁸Pu) is 5.2x10⁻³ cm. The range of a 5.59 MeV alpha particle in air is about 4.3 cm. Therefore, any waste material within about 4.3 cm of an alpha source could potentially receive alpha radiation. However, once an alpha particle strikes a material with a mass density of about 1 g/cm³, its range in that material would only be about 4.6x10⁻³ cm.

The range of beta particles is more difficult to calculate than the range of alpha particles. The path of a beta particle is very irregular and not as straight as that of heavy charged particles. A practical range, also called extrapolated range, for beta particles with energies up to 3 MeV can be estimated by the following equation (Liverhant 1960):

$$\text{Range}_\beta (\text{gram/cm}^2) = 0.546 * \text{Particle Energy (MeV)} - 0.108. \quad 3.7$$

For beta-emitting nuclides in TRU waste, the energies are typically 1 to 3 MeV. The range of a 1 MeV beta particle is 0.498 g/cm², and the range of a 3 MeV beta particle is 1.53 g/cm². In air ($\rho=1.2 \times 10^{-3}$ g/cm³), the range of a 1 MeV beta particle is about 365 cm and the range of a 3 MeV beta particle is about 1275 cm. In material with a mass density of 1 g/cm³, the range of a 1 MeV beta particle is about 0.44 cm and the range for a 3 MeV beta particle is about 1.53 cm. From a practical standpoint, the range of beta particles from radioactive decay is typically much larger than that of alphas, and $F_{P,\beta}$ may be assumed to be 1.0

Therefore, with $F_{P,\alpha}=F_{P,\beta}=F_{P,\gamma}=1$, the effective G value becomes:

$$G_{\text{eff}} = \lambda_\alpha \sum_M [F_{M,\alpha} \times G_{M,\alpha}] + \lambda_\beta \sum_M [F_{M,\beta} \times G_{M,\beta}] + \lambda_\gamma \sum_M [F_{M,\gamma} \times G_{M,\gamma}] \quad 3.8$$

In many instances, detailed information concerning the radionuclides and their concentrations in a waste material may be unavailable, and determination of the separate decay fractions (λ_α , λ_β , and λ_γ) may not be possible. For most waste types and waste configurations, a conservative approach is to assume that all decay energy is in the form of alpha decay, but the conservatism of this approach needs to be justified.

3. Hydrogen Generation Rates in Transuranic Waste

$$P_F = \frac{2 t_R (r + h)}{r h}$$

3.9

where: P_F is the particle fraction that can reach the plastic packaging materials;

t_R is the range of the particles in the waste material [cm];

r is the radius of the cylinder [cm]; and

h is the height of the cylinder [cm].

For example, a waste mass with an approximate volume of one gallon (with a radius of 7.62 cm (3.0 in.) and a height of 20.32 cm (8.0 in.)) has a $P_F=1.8 \times 10^{-3}$ for alpha particles and a $P_F=0.55$ for beta particles. Since the amount of material inserted into the product can be typically one gallon or more, these P_F values are considered conservative for most cases.

For gamma-emitting wastes, most of the gamma rays will escape the solidified mass. As a result of the penetrating nature of gamma rays and to a lesser extent beta particles, most of the gamma ray and beta particle energy would also penetrate through the plastic bags and only a very small fraction of the total gamma ray and beta particle energy deposited in the bags. This small fraction of gamma ray and beta particle energy deposited may be calculated, or conservatively, the fraction of beta and gamma decay energy that escapes the solidified waste and is deposited in the polymeric confinement layers (e.g., plastic bags that are usually polyethylene or polyvinylchloride) can be assumed to be 1.0.

3.3.2.1 Effective G Value for Solidified Aqueous Inorganic Absorbed Waste

Solidified Aqueous Inorganic Absorbed Waste may include any inorganic absorbents or solidification agents. The radionuclides may be present as particles or in solution encapsulated by the solidification materials. Because of the possibility of energy transfer between these inorganic materials and water, the fraction of available energy absorbed by the water is assumed to be 1.0.

For Solidified Aqueous Inorganic Absorbed Waste, the coefficients used in Equation 3.5 are summarized in Table 3.5.

Table 3.5 Coefficients for Calculation of Effective G(gas) for Solidified Aqueous Inorganic Absorbed Waste

Coefficient	Value	Coefficient	Value	Coefficient	Value
$F_{P, \alpha}$	1.0 ^a	$F_{water, \alpha}$	1.0 ^b	$F_{plastic, \alpha}$	1.8×10^{-3} ^d
$F_{P, \beta}$	1.0	$F_{water, \beta}$	1.0	$F_{plastic, \beta}$	0.55 ^e
$F_{P, \gamma}$	1.0	$F_{water, \gamma}$	1.0 ^c	$F_{plastic, \gamma}$	TBD ^f

^a A value < 1.0 may be justifiable for particles that have diameters that remain greater than ~ 10 μ m.

^b Due to energy transfer, all the alpha energy is assumed to be absorbed by the water.

^c A value of 1.0 is conservative; a calculated value less than 1.0 may be justifiable.

^d Valid estimate for inorganic solids with a surface area to volume ratio < 1.3 (min. volume 1 gallon, see Sec. 3.3.2).

^e Valid estimate for inorganic solids with a surface area to volume ratio < 1.3 (min. volume 1 gallon, see Sec. 3.3.2).

^f A calculated value less than 1.0 may be justified.

Using the coefficients in Table 3.5, the effective radiolytic G value for Solidified Aqueous Inorganic Absorbed Waste is:

3. Hydrogen Generation Rates in Transuranic Waste

Table 3.6 Coefficients for Calculation of Effective G(gas) for Solidified Aqueous Inorganic Particulate Waste

Coefficient	Value	Coefficient	Value	Coefficient	Value
$F_{P, \alpha}$	1.0 ^a	$F_{water, \alpha}$	1.0 ^b	$F_{plastic, \alpha}$	1.8×10^{-3} ^d
$F_{P, \beta}$	1.0	$F_{water, \beta}$	1.0	$F_{plastic, \beta}$	0.55 ^e
$F_{P, \gamma}$	1.0	$F_{water, \gamma}$	1.0 ^c	$F_{plastic, \gamma}$	TBD ^f

a A value < 1.0 may be justifiable for particles that have diameters that remain greater than ~ 10 μm .

b Due to energy transfer, all the alpha energy is assumed to be absorbed by the water.

c A value of 1.0 is conservative; a calculated value less than 1.0 may be justifiable.

d Valid estimate for inorganic solids with a surface area to volume ratio < 1.3 (min. volume 1 gallon, see Sec. 3.3.2).

e Valid estimate for inorganic solids with a surface area to volume ratio < 1.3 (min. volume 1 gallon, see Sec. 3.3.2).

f A calculated value less than 1.0 may be justifiable.

Substituting the coefficients in Table 3.6 into Equation 3.5, the effective radiolytic G value for Solidified Aqueous Inorganic Particulate Waste is obtained:

$$\begin{aligned}
 G_{\text{Solidified Aqueous Inorganic Particulate Waste}} = & \lambda_{\alpha} [(1.8 \times 10^{-3})(G(\text{plastic})) + (1.0)(G(\text{water}))] \\
 & + \lambda_{\beta} [(0.55)(G(\text{plastic})) + (1.0)(G(\text{water}))] \\
 & + \lambda_{\gamma} [(F_{plastic, \gamma})(G(\text{plastic})) + (F_{water, \gamma})(G(\text{water}))].
 \end{aligned} \quad 3.15$$

The effective G value for Solidified Aqueous Inorganic Particulate Waste that contains predominantly alpha-emitting radionuclides (i.e. $\lambda_{\beta} = \lambda_{\gamma} = 0$ in Equation 3.15) is given by:

$$\begin{aligned}
 G_{\text{Solidified Aqueous Inorganic Particulate Waste, } \alpha} = & \sum_M [(F_M \times G_M) \times F_P] \\
 = & \{ [(1.8 \times 10^{-3})(G(\text{plastic}))] + [(1.0)(G(\text{water}))] \} (1.0).
 \end{aligned} \quad 3.16$$

Using $G_{plastic, \alpha}(H_2) = 4.1$, $G_{plastic}(gas) = 4.1$ (based on the radiolysis of polyethylene), and $G_{plastic}(HCl) = 0.7$ (based on the radiolysis of polyvinylchloride), and $G_{water, \alpha}(H_2) = 1.6$ (based on the α -radiolysis of water), $G_{water}(gas) = 2.4$ (assuming oxygen and hydrogen are released from the radiolysis of water) in Equation 3.16, the effective G values for potentially flammable gas (H_2), HCl, and net gas for Solidified Aqueous Inorganic Particulate Waste that contains predominately alpha-emitting radionuclides can be estimated as:

$$G(H_2) = [(1.8 \times 10^{-3})(4.1) + (1.0)(1.6)](1.0) = 1.6 \quad 3.17$$

$$G(HCl) = [(1.8 \times 10^{-3})(0.7)](1.0) = 1.08 \times 10^{-3} = 0 \quad 3.18$$

$$G(\text{net gas}) = [(1.8 \times 10^{-3})(4.1) + (1.0)(2.4)](1.0) = 2.4. \quad 3.19$$

Note that the contributions to the effective G values from the radiolysis of the polymeric confinement layers are negligible for Solidified Aqueous Inorganic Particulate Waste.

3. Hydrogen Generation Rates in Transuranic Waste

Aqueous Inorganic Concreted Waste that contains predominately alpha-emitting radionuclides can be estimated as:

$$G(H_2)=[(1.8 \times 10^{-3})(4.1)+(0.3)(1.6)](1.0)=0.49 \quad 3.22$$

$$G(HCl)=[(1.8 \times 10^{-3})(0.7)](1.0)=1.08 \times 10^{-3}=0 \quad 3.23$$

$$G(\text{net gas})=[(1.8 \times 10^{-3})(4.1)+(0.30)(2.4)](1.0)=0.73. \quad 3.24$$

3.3.3 Effective G Values for Solid Inorganic Waste

Solid Inorganic Waste includes surface-contaminated solid inorganic materials, such as glass, metal, ceramics, and fiberglass. The waste materials must be dry and free of oil, grease, or other organics except for trace quantities (less than 1% by weight). The waste may be placed inside plastic bags (Solid Inorganic Waste in Plastic) or metal cans (Solid Inorganic Waste in Cans), and then in drums that have a rigid high-density polyethylene liner or other approved container.

No materials in Solid Inorganic Waste can radiolytically generate hydrogen. For Solid Inorganic Waste in Plastic, radiation that escapes the waste mass can cause radiation in the polymeric packaging (confinement layers). For Solid Inorganic Waste in Cans, gamma radiation that escapes the waste mass and penetrates the metal can could potentially cause radiolysis in any water or organic material (e.g., polymeric drum liner) that is outside the metal can confinement layer. However, any radiolysis that occurs due to gamma radiation that escapes the metal can is expected to be very low.

On average, the surface-contaminated inorganic waste will absorb half of the alpha decay energy escaping from the surface contamination. It is assumed that the other half of the decay energy is absorbed by the packaging materials. The inorganic materials are considered to generate no gas by radiolysis. For Solid Inorganic Waste in Plastic with polymeric confinement around the solid inorganic material, the polymeric material cannot have a $G(H_2)$ value that exceeds 4.1 (based on polyethylene) or a $G(HCl)$ value that exceeds 0.7 (based on PVC).

3.3.3.1 Effective G Values for Solid Inorganic Waste in Plastic

For Solid Inorganic Waste in Plastic, the coefficients used in Equation 3.5 to determine the effective G-value are summarized in Table 3.8.

Table 3.8 Coefficients for Calculation of Effective G(gas) for Solidified Aqueous Inorganic Particulate Waste

Coefficient	Value	Coefficient	Value	Coefficient	Value
$F_{P, \alpha}$	1.0 ^a	$F_{\text{water}, \alpha}$	0 ^b	$F_{\text{plastic}, \alpha}$	0.5 ^e
$F_{P, \beta}$	1.0	$F_{\text{water}, \beta}$	0 ^c	$F_{\text{plastic}, \beta}$	0.5 ^f
$F_{P, \gamma}$	1.0	$F_{\text{water}, \gamma}$	0 ^d	$F_{\text{plastic}, \gamma}$	0.5 ^g

^a A value < 1.0 may be justifiable for particles that have diameters that remain greater than ~ 10 μm .

^b No water or organics are allowed in Solid Inorganic Waste in Plastic.

^c No water or organics are allowed in Solid Inorganic Waste in Plastic.

^e No water or organics are allowed in Solid Inorganic Waste in Plastic.

^e Half of the decay energy from the surface contamination can interact with the packaging (e.g., plastic bags).

^f Half of the decay energy from the surface contamination can interact with the packaging (e.g., plastic bags); a value less than 0.5 may be justifiable.

3. Hydrogen Generation Rates in Transuranic Waste

The surface-contaminated organic waste or their organic packaging is assumed to absorb 100% of the available decay energy. The only gas generated by inorganic materials is oxygen, which would tend to oxidize the plastic packaging materials. Therefore, any inorganic materials present are considered to generate no gas by radiolysis.

Radiolysis of the solid organic materials (typically plastic) bounds the radiolytic gas generation for Solid Organic Waste. For Solid Organic Waste, the coefficients used in Equation 3.5 to determine the effective G-value are summarized in Table 3.9.

Table 3.9 Coefficients for Calculation of Effective G(gas) for Solid Organic Waste

Coefficient	Value	Coefficient	Value
$F_{P, \alpha}$	1.0 ^a	$F_{\text{plastic}, \alpha}$	1.0 ^b
$F_{P, \beta}$	1.0	$F_{\text{plastic}, \beta}$	1.0 ^c
$F_{P, \gamma}$	1.0	$F_{\text{plastic}, \gamma}$	1.0 ^{d, e}

^a A value <1.0 may be justifiable for particles that have diameters that remain greater than ~ 10 μm .

^{b, c, d} Energy transfer is assumed to occur.

^e A value of 1.0 is conservative; a calculated value less than 1.0 may be justified.

Using the coefficients from Table 3.9 in Equation 3.5, the effective radiolytic G value for Solid Organic Waste is:

$$G_{\text{Solid Organic Waste}} = \lambda_{\alpha} [(1.0)(G_{\text{Solid Organic}})] + \lambda_{\beta} [(1.0)(G_{\text{Solid Organic}})] + \lambda_{\gamma} [(F_{\text{plastic}, \gamma})(G_{\text{Solid Organic}})] \quad 3.30$$

The effective G value for Solid Organic Waste that contains radionuclides which are mainly alpha-emitters (i.e. $\lambda_{\beta}=\lambda_{\gamma}=0$) is:

$$G_{\text{Solid Organic Waste}, \alpha} = (1.0)(G(\text{solid organic})). \quad 3.31$$

Therefore, using the G values of $G(\text{H}_2)=4.1$ (based on the radiolysis of polyethylene), $G(\text{HCl})=0.7$ (based on the radiolysis of polyvinylchloride), and $G(\text{net gas})=10.2$ (based on the radiolysis of cellulose) for waste containing radionuclides that are predominantly alpha-emitters, the effective G-values for Solid Organic Waste are:

$$G(\text{H}_2)=[(1.0)(4.1)](1.0)=4.1 \quad 3.32$$

$$G(\text{HCl})=[(1.0)(0.7)](1.0)=0.7 \quad 3.33$$

$$G(\text{net gas})=[(1.0)(10.2)](1.0)=10.2. \quad 3.34$$

3.3.5 Summary of the Effective G Values for Various Waste Types When the Radionuclides are Primarily Alpha-Emitters

Table 3.10 summarizes the radiolytic G values for hydrogen, hydrogen chloride, and net gas generation for the various waste types discussed above.

4. CALCULATION OF HYDROGEN CONCENTRATION FOR VARIOUS PACKAGING CONFIGURATIONS

4.1 Modeling Hydrogen Concentration in TRU Waste Transportation Containers

The predominant source of hydrogen in a TRU waste transportation package is typically from the radiolysis of the hydrogenous material(s) in the contents. For contents that include significant gamma-emitting nuclides or for contents that are adjacent to hydrogenous confinement materials, radiolysis of the polymeric confinement layers can also contribute significantly to the total hydrogen generation rate.

As hydrogen is generated, it could potentially accumulate within a confinement region to form a flammable mixture. This accumulation will occur if the release rate of hydrogen from that barrier is less than the sum of the generation rate within the region and the rate of hydrogen entering the confinement barrier. Parameters that govern the release of hydrogen from the various confinement and containment barriers in TRU waste transportation containers include:

- (a) Waste packaging configuration (i.e., the number and type of confinement and containment layers surrounding the waste),
- (b) Rate of hydrogen generation within the waste and confinement layers,
- (c) Release rates of hydrogen from each of the confinement and containment layers,
- (d) Temperature of the waste and the confinement components,
- (e) Void volume within the various product containers, confinement layers, and containment vessel(s), and
- (f) Duration of the shipping period (normally assumed to be a maximum of one year).

The release rate of hydrogen through a given confinement barrier is a combination of the rate of hydrogen diffusion through any opening(s) or leakage path(s) in the barrier and the rate of hydrogen permeation through the barrier material. Some confinement materials, such as metal product cans (food pack cans) and glass containers, do not allow significant hydrogen permeation and any release of hydrogen is due to gas escaping through leakage paths. However, for other confinement materials, such as polymeric bags and polymeric drum liners, the hydrogen permeation rate can be significant. The hydrogen permeation rate through plastic bags is often on the order of the hydrogen diffusion rate through the small leakage paths in the twist-and-tape or fold-and-tape closures of plastic bags (NRC Docket No. 71-9218, Aug. 11, 1999). In general, the number of confinement layers should be minimized and the hydrogen permeability of the confinement layers should be maximized to limit the rate of hydrogen accumulation in the innermost confinement barrier, which is typically the region of highest hydrogen concentration.

The most common confinement barrier materials in a TRU waste transportation package are polymeric bags and metal cans. Some TRU wastes are placed in metal product cans and then "bagged out" by placing the metal can in a plastic bag. This bagged can may then be placed in one or more bags or in a second can that is bagged. Other TRU wastes may be placed directly in plastic bags.

R is the gas law constant [82.05 atm-cm³/gmol-K];

T is the gas temperature [K];

P is the gas pressure [atm]; and

t is the thickness of the confinement barrier [cm].

Substituting for the hydrogen concentration gradient into the Equation 4.1 gives:

$$T_D = \left[\frac{D_{H_2} \pi d^2 P (x_{H_2, in} - x_{H_2, out})}{4 t R T} \right] \quad 4.3$$

To obtain conservative estimates of the effective hydrogen transport rate due to diffusion, the above equation should be calculated using: (1) the minimum leakage path cross-sectional area, (2) the coefficient for hydrogen diffusion in air at the minimum temperature, and (3) a pressure of one atmosphere.

4.1.2 Permeation of Hydrogen Through Packaging Materials

The permeability of a material to hydrogen is quantified as the material's hydrogen permeability coefficient. Permeability may be defined as the number of moles of gas passing per unit time through a material of unit area, which is of unit thickness under a unit partial pressure gradient at a specified temperature. Typical units for permeability are (mole-cm)/(s-cm²-mmHg). The permeability rate depends on the material type, material thickness, the material's history (i.e., absorbed dose), the concentration driving force, and temperature.

Two materials that are commonly used as polymeric confinement barriers (plastic bags) in TRU waste transportation packagings are polyvinyl chloride (PVC) and polyethylene (PE). In addition to material type, permeability also depends on the additives in the materials.

The dose absorbed by a polymeric confinement material may influence its permeability to gases. Although gamma doses up to 800 krad seem to have no effect of the permeability of PE and PVC to N₂, O₂, CO₂ and H₂O, and the crosslinking in the polymers caused by gamma ray absorption has been shown to not cause significant changes in the permeability (NRC Docket No. 71-9218, Aug. 11, 1999), preliminary tests performed on waste drums that had been stored for fifteen years indicate that the hydrogen permeability rates through both PE and PVC were higher than the rates through new plastic samples (Varsanyi 1975). For TRU waste materials that were placed in polymeric confinement layers recently or when the polymeric confinement layers have not absorbed a significant dose, the permeability rate of new confinement materials may be used for modeling purposes. For TRU waste materials that have been in particular confinement layers for a significant period of time or for cases where the confinement materials have absorbed a significant dose, measurements can be performed on the radiation-damaged confinement material to obtain the appropriate permeability coefficient for modeling purposes. However, if it is known that the confinement barriers in a package have a higher permeability than new material, modeling the hydrogen release with the properties of the new material should yield conservative results for the hydrogen concentration within the inner-most confinement layer.

Permeabilities are highly temperature dependent and this dependence can be represented with an exponential Arrhenius-type equation (Varsanyi 1975):

$$P = \exp(-E_p/RT) \quad 4.4$$

$$n_{H_2} = \left(\frac{D_H}{100} \right) \left(\frac{G(H_2)}{A_N} \right) (t) = \left(\frac{D_H}{100} \right) \left(\frac{\alpha G(\text{net gas})}{A_N} \right) (t) \quad 4.7$$

where: $n_{\text{net gas}}$ is the number of moles of gas generated [gmol];
 $n_{\text{flam gas}}$ is the number of moles of flammable gas generated [gmol];
 D_H is the decay heat that is absorbed by the radiolytic materials [eV/s];
 $G(\text{flam gas})$ is the radiolytic G value for flammable gas [molecules/100 eV];
 $G(\text{net gas})$ is the radiolytic G value for net gas generation [molecules/100 eV];
 t is the time that the container has been sealed [s];
 A_N is Avagadro's number [6.023×10^{23} molecules/gmol]; and
 α is the fraction of $G_R(\text{net gas})$ that is equivalent to $G_R(\text{flam gas})$.

Using the above expressions, the mole fraction hydrogen, X_{H_2} , as a function of time is:

$$X_{H_2}(t) = \frac{n_{H_2}}{n_0 + n_{\text{net gas}}} = \frac{\left(\frac{D_H}{100} \right) \left(\frac{\alpha G(\text{netgas})}{A_N} \right) (t)}{\left(\frac{P_0 V}{R_g T_0} \right) + \left(\frac{D_H}{100} \right) \left(\frac{G(\text{netgas})}{A_N} \right) (t)} \quad 4.8$$

where: P_0 is the pressure when the container was sealed [atm];
 T_0 is the temperature when the container was sealed [K];
 V is the container void volume [cm^3];
 R_g is the gas law constant [$82.05 \text{ cm}^3 \cdot \text{atm} / \text{gmol} \cdot \text{K}$]; and
 n_0 is the initial number of gas moles in the container when the vessel was closed [gmol].

4.2.1.2 Hydrogen Gas Concentration in a Single Rigid Leaking Enclosure

An analysis is made of the hydrogen mole fraction as a function of time for an enclosure wherein hydrogen is being generated and the escape of hydrogen from the enclosure occurs by diffusion. The hydrogen mole balance for this case is:

$$\frac{d(Xn)}{dt} = R_M - T(X - X_s) \quad 4.9$$

where: n is the total number of gas moles within the enclosure [gmol];
 X is the hydrogen gas mole fraction;
 R_M is the molar hydrogen generation rate [gmol H_2 /s];
 T is the effective transport rate of hydrogen from the enclosure [gmol H_2 /s mole fraction];

C_A is the flammable gas concentration of the gas escaping the container [gmol/cm³];

V is the void volume in the container [cm³]; and

t is the time [s].

Separating variables and integrating yield:

$$C_A = C_{A0} \left[1 - \exp\left(\frac{-tQ}{V}\right) \right]. \quad 4.14$$

For an example calculation of the hydrogen concentration in a single semi-open rigid container with its contents undergoing radiolysis, see Example #2, Appendix F.

4.2.2 Simple Nested Enclosures

This section develops representative methods for modeling the hydrogen concentration as a function of time for various numbers of nested enclosures used to represent nested confinement layers (e.g., plastic bags, plastic drum liners, food product cans) and containment layers.

4.2.2.1 Hydrogen Gas Concentration in a Rigid Leaking Enclosure Nested Within a Rigid Non-Leaking Enclosure

Consider a rigid leaking enclosure holding radioactive material that is nested within a second rigid nonleaking enclosure. The radioactive material within the inner enclosure is radiolytically generating hydrogen. If the hydrogen escapes the inner enclosures only by diffusion, the hydrogen mole balance can be formed as follows:

$$\begin{aligned} \frac{d(n_1 X_1)}{dt} &= R_M - T_1(X_1 - X_2) \\ \frac{d(n_2 X_2)}{dt} &= T_1(X_1 - X_2) \end{aligned} \quad 4.15 \text{ a,b}$$

where: n_1 is the number of gas moles within enclosure #1 (inner enclosure) as a function of time
($=n_{0,1} + n_{H2,1}$) [gmol];

n_2 is the number of gas moles within enclosure #2 (outer enclosure) as a function of time
($=n_{0,2} + n_{H2,2}$), (not including gas within enclosure #1) [gmol];

$n_{0,1}$ is the initial number of gas moles within enclosure #1 [gmol];

$n_{0,2}$ is the initial number of gas moles within enclosure #2 [gmol];

$n_{H2,1}$ is the number of hydrogen gas moles within enclosure #1 as a function of time [gmol];

$n_{H2,2}$ is the number of hydrogen gas moles within enclosure #2 as a function of time [gmol];

X_1 is the hydrogen gas mole fraction within enclosure #1;

X_2 is the hydrogen gas mole fraction within enclosure #2;

For the check that Equations 4.19 and 4.20 are the solutions to the differential Equations 4.18a and 4.18b, see Example #3, Appendix F. For an example calculation of the hydrogen gas concentration in a rigid leaking enclosure nested within a rigid non-leaking enclosure, see Example #4, Appendix F.

4.2.2.2 Hydrogen Gas Concentration in Two Nested Rigid Leaking Enclosures

Consider a rigid leaking enclosure holding radioactive material that is nested within a second rigid leaking enclosure. The radioactive material within the inner enclosure is radiolytically generating hydrogen. If the hydrogen escapes the inner enclosures only by diffusion, and the quasi-steady assumption that the total gas moles in each enclosure remain relatively unchanged is used, the hydrogen mole balance can be formed as follows:

$$\begin{aligned} n_1 \frac{dX_1}{dt} &= R_M - T_1(X_1 - X_2) \\ n_2 \frac{dX_2}{dt} &= T_1(X_1 - X_2) - T_2(X_2 - X_a) \end{aligned} \quad 4.21 \text{ a,b}$$

or

$$\begin{aligned} \frac{dX_1}{dt} &= S - A(X_1 - X_2) \\ \frac{dX_2}{dt} &= B(X_1 - X_2) - C(X_2 - X_a) \end{aligned} \quad 4.22 \text{ a,b}$$

where: $S = R_M/n_1$; $A = T_1/n_1$; $B = T_1/n_2$; $C = T_2/n_2$;

n_1 is the number of gas moles within enclosure #1 (inner enclosure) when the enclosure was sealed [gmol];

n_2 is the number of gas moles within enclosure #2 (outer enclosure) when the enclosure was sealed [gmol];

X_1 is the hydrogen gas mole fraction within enclosure #1;

X_2 is the hydrogen gas mole fraction within enclosure #2;

T_1 is the effective rate of hydrogen transport through the wall of enclosure #1 [gmol H₂/s-mole fraction];

T_2 is the effective rate of hydrogen transport through the wall of enclosure #2 [gmol H₂/s-mole fraction];

t is the time [seconds]; and

X_a is the hydrogen mole fraction in the ambient environment (outside enclosure #2).

For an outer enclosure leaking to an ambient environment that contains no hydrogen, then $X_a=0$ and the equations reduce to:

$$n_1 \frac{dX_1}{dt} = R_M - T_1(X_1 - X_2)$$

$$n_2 \frac{dX_2}{dt} = T_1(X_1 - X_2) - T_2(X_2 - X_3)$$

4.26 a,b,c

$$n_3 \frac{dX_3}{dt} = T_2(X_2 - X_3),$$

or

$$\frac{dX_1}{dt} = S - A(X_1 - X_2)$$

$$\frac{dX_2}{dt} = B(X_1 - X_2) - C(X_2 - X_3)$$

4.27 a,b,c

$$\frac{dX_3}{dt} = D(X_2 - X_3)$$

where: $S = R_M/n_1$; $A = T_1/n_1$; $B = T_1/n_2$; $C = T_2/n_2$; $D = T_2/n_3$;

n_1 is the number of gas moles within enclosure #1 (inner enclosure) when the enclosure was sealed [gmol];

n_2 is the number of gas moles within enclosure #2 (secondary enclosure) when the enclosure was sealed [gmol];

n_3 is the number of gas moles within enclosure #3 (outer enclosure) when the enclosure was sealed [gmol];

X_1 is the hydrogen gas mole fraction within enclosure #1;

X_2 is the hydrogen gas mole fraction within enclosure #2;

X_3 is the hydrogen gas mole fraction within enclosure #3;

T_1 is the effective rate of hydrogen transport through the wall of enclosure #1 [gmol H₂/s-mole fraction];

T_2 is the effective rate of hydrogen transport through the wall of enclosure #2 [gmol H₂/s-mole fraction]; and

t is the time [seconds].

The initial conditions for the above three coupled ordinary differential equations are: $X_1(0)=0$; $X_2(0)=0$; and $X_3(0)=0$.

4.2.2.4 Hydrogen Gas Concentration in Three Nested Rigid Leaking Enclosures

Consider a rigid leaking enclosure holding radioactive material that is nested within a second rigid leaking enclosure, which is in turn nested within a third rigid leaking enclosure. The radioactive material within the inner enclosure is radiolytically generating hydrogen. If the hydrogen escapes the inner and

$$\frac{dX_1}{dt} = S - A(X_1 - X_2)$$

$$\frac{dX_2}{dt} = B(X_1 - X_2) - C(X_2 - X_3)$$

4.30 a,b,c

$$\frac{dX_3}{dt} = D(X_2 - X_3) - E(X_3).$$

4.2.2.5 Hydrogen Gas Concentration in Multiple Nested Enclosures: Generalized Approach

Generalized Approach for a Single Contents

Consider radioactive material that is nested within multiple enclosures. Although differential equations can be developed and solved numerically to determine the hydrogen concentration in all void spaces between the various confinement and containment layers, the hydrogen gas concentration within the inner-most confinement layer is typically limiting (bounding). It is convenient (and yields bounding results for the hydrogen concentration within the inner-most confinement layer) to group the various confinement layers together to obtain an effective resistance to hydrogen flow that represents the sum of the resistances due to all the confinement layers. Using such an approach, the effective rate of hydrogen transport through the four confinement layers is:

$$T_{\text{eff}} = \frac{T_1 T_2 T_3 T_4}{T_1 + T_2 + T_3 + T_4}. \quad 4.31$$

Similarly, for N confinement layers, the effective rate of hydrogen transport through the N layers is:

$$T_{\text{eff}} = \frac{\prod_{i=1}^N T_i}{\sum_{i=1}^N T_i}. \quad 4.32$$

Using this effective rate of hydrogen transport, the hydrogen concentrations associated with a contents nested within N confinement layers and then placed in a containment vessel (surrounded by an atmosphere that contains no hydrogen) have the form of Equations 4.23a,b:

$$\frac{dX_1}{dt} = S - A(X_1 - X_2)$$

$$\frac{dX_2}{dt} = B(X_1 - X_2) - C(X_2),$$

4.33 a,b

where: $S = R_M/n_1$; $A = T_{\text{eff}}/n_1$; $B = T_{\text{eff}}/n_2$; $C = T_2/n_2$;

n_1 is the number of gas moles within the inner-most confinement layer [gmol];

n_2 is the number of gas moles between the outer-most confinement layer and the containment vessel (it is assumed that the volume between the N confinement layers is zero) [gmol];

and the solution for the hydrogen concentration as a function of time for the volume between the outer-most confinement layer and the containment vessel is:

$$X_C(t) = \frac{-BS}{(A+B)^2} + \frac{BS \exp[-t(A+B)]}{(A+B)^2} + \frac{BS t}{(A+B)} \quad 4.36$$

where: $S = (R_M/n_1)$; $A = (T_{eff}/n_1)$; and $B = (T_{eff}/n_C)$.

Generalized Approach for Multiple Contents

For a non-leaking containment vessel holding N contents each with multiple layers of confinement, the differential equations describing the hydrogen concentration are:

$$\begin{aligned} n_1 \frac{dX_1}{dt} &= R_{M,1} - T_{eff,1}(X_1 - X_C), \\ n_2 \frac{dX_2}{dt} &= R_{M,2} - T_{eff,2}(X_2 - X_C), \\ n_3 \frac{dX_3}{dt} &= R_{M,3} - T_{eff,3}(X_3 - X_C), \\ &\dots\dots n_N \frac{dX_N}{dt} = R_{M,N} - T_{eff,N}(X_N - X_C), \text{ and} \\ n_C \frac{dX_C}{dt} &= T_{eff,1}(X_1 - X_C) + T_{eff,2}(X_2 - X_C) + T_{eff,3}(X_3 - X_C) + \dots\dots + T_{eff,N}(X_N - X_C) \end{aligned} \quad 4.37 \text{ a,b},\dots,n$$

where: n_i is the number of gas moles initially in the multiple confinement layers around payload i [gmol];

n_C is the number of gas moles initially in the volume between the outer confinement layers around each payload and the containment vessel [gmol];

X_i is the hydrogen mole fraction within the inner-most confinement layer surrounding payload i;

X_C is the hydrogen mole fraction between the outer-most confinement layer of each payload and the containment vessel; and

$T_{eff,i}$ is the effective rate of hydrogen transport across the multiple confinement layers around payload i [gmol H₂/s-mole fraction].

If it can be assumed that: (a) all the contents are essentially identical, (b) that the hydrogen generation rate from each of the contents is the same (i.e., $R_{M,1} = R_{M,2} = R_{M,3} = \dots = R_{M,N} = R_M$), (c) that the number and type of confinement layers around the N contents are the same (i.e., $T_{eff,1} = T_{eff,2} = T_{eff,3} = \dots = T_{eff,N} = T_{eff}$ and $n_1 = n_2 = n_3 = \dots = n_N$), then the set of differential equations in 3.2.37n reduces to:

$$\begin{aligned} n_1 \frac{dX_1}{dt} &= R_M - T_{eff}(X_1 - X_C) \\ n_C \frac{dX_C}{dt} &= N T_{eff}(X_1 - X_C), \end{aligned} \quad 4.38 \text{ a,b}$$

which have the form:

where: R_M is the molar radiolytic gas generation rate [gmol/s];
 D_H is the contents decay heat [eV];
 G (net gas) is the effective radiolytic net gas G_R value [molecules gas/100 eV]; and
 A_N is Avagadro's number [6.023×10^{23} molecules/gmol].

Using the radiolytic gas production rate, the ideal gas law can be used to describe the container pressure as a function of time:

$$P_u(t) = \frac{(n_o + R_M t) R_g T}{V} \quad 4.45$$

where: $P_u(t)$ is the container pressure as a function of time [atm];
 n_o is the initial number of moles of gas inside the container [gmol];
 t is the time that the container has been sealed [s];
 R_g is the gas law constant [$82.05 \text{ cm}^3 \cdot \text{atm} / \text{gmol} \cdot \text{K}$];
 T is the container temperature [K]; and
 V is the container void volume [cm^3].

If the container was initially sealed at a pressure P_o and a temperature T_o , then the initial number of gas moles, n_o , is:

$$n_o = \frac{P_o V}{R_g T_o} \quad 4.46$$

Substituting the expression for the initial number of gas moles and for the radiolytic gas production rate, the pressure in a single non-leaking enclosure is:

$$P(t) = \left[P_o \left(\frac{T}{T_o} \right) \right] + \left[\left(\frac{D_H}{100} \right) \left(\frac{G(\text{net gas})}{A_N} \right) \left(\frac{R_g T}{V} \right) t \right] \quad 4.47$$

For an example calculation of the pressure in a single rigid non-leaking container with its contents undergoing radiolysis, see Example #6, Appendix F.

4.3.2 Pressure in a Single Rigid Leaking Enclosure

Consider a container holding radioactive contents that has a void volume, V , where gas is generated at a rate, R_M , which is the rate of radiolytic gas generation. The container has a small leak hole with a diameter, D , through which gas leaks out to the environment at a rate dependent on the gas pressure within the container.

As shown above, the decay heat, D_H , that is absorbed by the radiolytic material and the effective radiolytic G -value of the material determines the gas generation rate:

$$\frac{dP_u}{dt} = \left(\frac{R_g T R_M}{V} \right) - \left[(F_C + F_M)(P_u - P_d) \left(\frac{P_u + P_d}{2P_u} \right) \left(\frac{P_u}{V} \right) \right] \quad 4.53$$

or after rearranging:

$$\frac{dP_u}{dt} = \left(\frac{R_g T R_M}{V} \right) + \left[\left(\frac{F_C + F_M}{2V} \right) P_d^2 \right] - \left[\left(\frac{F_C + F_M}{2V} \right) P_u^2 \right]. \quad 4.54$$

This equation has the form:

$$\frac{dP_u}{dt} + \Omega P_u^2 = \Phi \quad 4.55$$

$$\text{where: } \Omega = \left[\frac{(F_C + F_M)}{2V} \right] \quad \text{and} \quad \Phi = \left(\frac{R_g T R_M}{V} \right) + \left(\frac{(F_C + F_M) P_d^2}{2V} \right),$$

and F_m is treated as a constant even though it is a function of the average pressure $[(P_u + P_d)/2]$. Since the average pressure is greater than or equal to one atmosphere (for $P_d = 1$ atm), using an average pressure of 1 atm for the calculation of F_m would bound the rate of gas release from a container. On the other hand, neglecting the contribution of molecular flow to the total flow from a container would bound the pressure in the container.

Separating variables in the above differential equation gives:

$$\frac{dP_u}{\left(\frac{\Phi}{\Omega} \right) - P_u^2} = \frac{dP_u}{\Psi - P_u^2} = \Omega dt \quad 4.56$$

$$\text{where: } \Psi = \frac{\Phi}{\Omega} = \frac{\left(\frac{R_g T R_M}{V} \right) + \left(\frac{(F_C + F_M) P_d^2}{2V} \right)}{\frac{(F_C + F_M)}{2V}} = \left(\frac{2R_g T R_M}{F_C + F_M} \right) + P_d^2.$$

Integrating the above equation and rearranging gives:

$$\tanh^{-1} \left(\frac{P_u}{\sqrt{\Psi}} \right) = (\Omega \sqrt{\Psi}) t + C, \text{ where } \Omega, \Psi, \text{ and } C \text{ can be considered constants} \quad 4.57$$

Applying the initial condition that $P_u = P_{u,0}$ at $t=0$, C is determined:

$$C = \tanh^{-1} \left(\frac{P_{u,0}}{\sqrt{\Psi}} \right). \quad 4.58$$

After substituting for C and rearranging, the gas pressure inside the container as a function of time is:

4.4 Time to Reach the Lower Flammability Limit for Hydrogen in Transuranic Waste Transportation Packages

This section addresses representative methods for determining the potential flammability of gaseous mixtures that may be present in TRU waste transportation packages. After a general discussion of flammability limits, methods are presented to predict the time for reaching the lower flammability limit, particularly for hydrogen, within various layers of confinement of TRU waste transportation packages. The methods are based on limiting hydrogen to a concentration below its lower flammability limit in air during the shipping period. Typically the shipping period is a maximum of one year, which is consistent with the time period for determining the maximum normal operating pressure. For special cases, however, alternative shipping periods may be justified. For such justified cases, the shipping period may be defined as equal to one-half the time it takes the hydrogen to reach its lower flammability limit.

4.4.1 Flammability Limits

The flammability limit of a gas mixture comprised of a flammable gas and a gaseous oxidant represents a borderline composition; a slight change in one direction produces a flammable mixture, in the other direction a nonflammable mixture. There are two limits of flammability, a lower and a higher, for each fuel/oxidant pair. The lower limit corresponds to the minimum amount of combustible gas and the higher or upper limit to the maximum amount of combustible gas capable of conferring flammability on the mixture. Mixtures within these limits liberate enough energy on combustion of any one layer to ignite the neighboring layer of unburned gas and are therefore capable of self-propagation of flame; others mixtures are not.

4.4.1.1 Hydrogen Flammability Limits

Flames in mixtures of hydrogen and air are exceedingly pale; the flame in a limit mixture is almost invisible, even in a completely darkened room. Many experiments have been performed to determine the lower and upper flammability limits for hydrogen in air (Coward, 1952). A variety of geometrical configurations and ignition methods have been used for the reaction chamber. When using a vertically-oriented cylindrically-shaped reaction chamber, it was found that ignition at the top of the chamber (downward flame propagation) resulted in different results for the flammability limits compared with igniting the gases from the bottom of the chamber (upward flame propagation). A lower flammability limit of 4.1 volume percent hydrogen in air was measured for upward flame propagation in cylindrical tubes with diameters larger than about 2 inches. However, when the tube diameter was decreased to 0.8 inches, the lower flammability limit was 5.1 volume percent hydrogen. For horizontal flame propagation, the lower flammability limit for hydrogen in air was about 6.7 volume percent hydrogen, and for downward flame propagation the lower flammability was about 9 volume percent hydrogen.

For purposes of this document, the lower flammability limit for hydrogen in air is taken as 5 volume percent hydrogen. This value is considered appropriate based on the methods presented here, which are intended to provide a simplified analytical approach that is adequately conservative.

Increasing the pressure has only a marginal effect of the lower flammability limit for hydrogen in air. Some experiments have shown a slight increase (~ 2 volume percent) in the lower flammability limit as the pressure is increased from 1 to 5 atmospheres, however, other experiments have observed no change in the lower limit for pressures from 0.5 to 4 atmospheres.

An increase in temperature causes the lower limit to approach its lower bounding value, whereas an increase in temperature causes the upper limit to increase (i.e., at 540°C a 90.45 volume percent hydrogen mixture was ignited).

$G(\text{net gas})$ is the radiolytic G value for net gas generation [molecules/100 eV];

R_g is the gas law constant [$82.05 \text{ cm}^3 \cdot \text{atm}/\text{gmol} \cdot \text{K}$];

T_0 is the temperature when the container was sealed [K]; and

α is the mole fraction of the gas generated by radiolysis that is hydrogen.

From Equation 4.66, it is clear that α must be greater than 0.05 to yield reasonable results. From a physical perspective, if α is less than 0.05, a mixture of 5 volume percent hydrogen will never exist inside the container. Conservative estimates of the time to reach 5 volume percent hydrogen in the container can be obtained by setting α equal to 1.0.

4.4.2.2 Single Rigid Leaking Enclosures

For single rigid leaking enclosures, the hydrogen mole fraction as a function of time is given by Equation 4.71. Setting the hydrogen mole fraction in this equation to 0.05 (the lower flammability limit) and solving for time yields the time necessary for the gas mixture inside the vessel to reach 5 volume percent hydrogen:

$$t_{s_0} = \frac{-n}{T} \ln \left(1 - \frac{0.05 T}{R_M} \right) \quad 4.67$$

where: n is the initial number of moles of gas inside the container [gmol];

T is the rate of hydrogen transport from the enclosure [$\text{gmol H}_2/\text{s} \cdot \text{mole fraction}$]; and

R_M is the molar hydrogen generation rate [$\text{gmol H}_2/\text{s}$].

Equation 4.67 is valid only for cases where $(0.05 T) < R_M$. The initial number of gas mole inside the container when it is sealed, n , is calculated using the ideal gas equation along with the (i.e., $n = (P_0 V)/(R_g T_0)$).

4.4.3 Simple Nested Enclosures

The governing equations for the hydrogen mole fraction for simple nested enclosures are described in Section 4.2.2. The closed-form solutions giving the hydrogen mole fraction as a function of time for a rigid leaking enclosure nested within a rigid non-leaking enclosure are given by Equations 4.19 and 4.20. The closed-form solutions given the hydrogen mole fraction as a function of time for two nested rigid leaking enclosures are given by Equations 4.2.24 and 4.25. Since these equation cannot be solved explicitly for time, it is necessary to use a graphical approach, a trial-and-error, or a numerical iterative approach to determine the time necessary to reach a given hydrogen mole fraction. The simplest approach is to plot the solution for the hydrogen mole fraction as a function of time for the region of interest and to graphically determine the time that corresponds to the hydrogen mole fraction of interest. For an example calculation of the hydrogen gas concentration in a package containing radioactive material nested with three confinement layers and a containment vessel, see Example #9 in Appendix F.

6. SUMMARY

This document addresses hydrogen generation in TRU waste transportation packages. Four general hydrogen-generating mechanisms are considered: (1) chemical reaction, (2) thermal degradation, (3) biological metabolism, and (4) radiolysis. General information and guidelines are given for the first three mechanisms, with the focus of the report on hydrogen generation due to radiolysis.

The report provides methodologies for estimating the hydrogen generation in TRU waste due to radiolysis. Bounding $G(H_2)$ -values are determined for common types of TRU waste. Equations are developed that allow prediction of hydrogen concentration as a function of time for various TRU waste content types and packaging configurations. Also, equations are developed that allow prediction of the time required to reach a given hydrogen concentration for simple packaging configurations.

General guidelines are provided for limiting the hydrogen generation and accumulation in TRU waste transportation packages.

7. References

- Bohm, G. G. A. "Radiation Chemistry of Elastomers," in *The Radiation Chemistry of Macromolecules*, Vol. II, ed. M. Dole, Academic Press, New York, 1973.
- Bohm, G. "Radiation Chemistry," *Rubber Chem. Tech.*, 55(1982)575-666.
- Bolt, R. O. and J. G. Carroll, *Radiation Effects on Organic Materials*, Academic Press, New York, 1963.
- Bonzon, L. L. et al., "Status report on Equipment Qualification Issues—Research and Resolution," Sandia National Laboratories, NUREG/CR-4301, SAND85-1309, November 1986.
- Burnay, S. G. "Comparative Evaluation of α and γ Radiation Effects in a Bitumenisate," *Nuclear and Chemical Waste Management*, 7(1987)107-127.
- Burns, W. G. and H. E. Sims, "Effect of Radiation Type in Water Radiolysis," *J. Chem. Soc. Faraday Trans. I* 77(1981)2809-2813.
- Busfield, W. K. et al., "Radiation Degradation of Poly(styrene-co-Methylmethacrylate). 2. Protective Effects of Styrene on Volatile Products, Chain Scission and Flexural Strength," *Polymer*, 23(1982)431-434.
- Carniti, P. et al., "Polystyrene Thermodegradation. 2. Kinetics of Formation of Volatile Products," *Ind. Eng. Chem. Res.*, 30(1991)1624-1629.
- Cember, H., *Introduction to Health Physics*, Pergamon Press, New York, 1978.
- Chapiro, A., *Radiation Chemistry of Polymeric Systems*, Interscience, Publishers, New York, 1962.
- Characklis, W. G., "Bacterial Regrowth in Distribution Systems," American Water Works Assoc. Research Foundation Research Rep., American Water Works Assoc., Denver, CO, 1988.
- Chen, T. H. et al., "Radiolysis of Chloroform and Carbon Tetrachloride," *J. Phys. Chem.*, 64(1960) 1023- 1025.
- Coward, H. F. and G. W. Jones, "Limits of Flammability of Gases and Vapors," Bulletin 503, Bureau of
- Cowell, W. R. *Sources and Development of Mathematical Software*, Prentice Hall, New York, 1984.
- Dalton, F. L. et al., "Gas Yields from Electron-Irradiated Cotton Cellulose," *Nature*, 200, pp. 862-864, 1963.
- Deanin, R. D. *Polymer Structure, Properties and Applications*, Chancers Books, Boston, 1972.
- Dole, L. R. and H. A. Friedman, "Radiolytic Gas Generation from Cement-Based Waste Hosts for DOE Low-Level Radioactive Wastes," preprint of a presentation at the Symposium on the Effects of Radiation on Materials, Seattle, Washington, June 1986.
- Dole, M., "Effects of Radiation Environments on Plastics," in *The Effects of Hostile Environments on Coatings and Plastics*, ed. D.P. Garner, American Chemical Society, Washington D.C., 1983, pp. 17-24.
- Dole, M., "Polyoxymethylene," in *The Radiation Chemistry of Macromolecules*, Vol. II, ed. M. Dole, Academic Press, New York, 1973.
- Ershov, B. G. et al., "Mechanism of the Radiation Chemical Conversions of Cellulose," translated from *Khimiya Vysokikh Energii*, 20(1986)142-147.

7. References

- Johnson, E. R. *The Radiation-Induced Decomposition of Inorganic Molecular Ions*, Gordon and Breach Science Publishers, New York, 1970.
- Joret, J. C., Y. Levi, T. Dupin, and M. Gilbert, "Rapid Method for Estimating Biodegradable Organic Carbon in Water," Proc. Annu. Conf. American Water Works Assoc., Denver, CO, 1988.
- Kalia, V. C. and A. P. Joshi, "Conversion of Waste Biomass (Pea-Shells) into Hydrogen and Methane Through Anaerobic-Digestion," *Bioresources Technology*, 53:2(1995)165-168.
- Kazanjian, A. R. and A. K. Brown, "Radiation Chemistry of Materials Used in Plutonium Processing," The Dow Chemical Company, Rocky Flats Division, RFP-1376, December 1969.
- Kazanjian, A. R. and D.R. Horrell, "The Radiation-Induced Oxidation of Trichloroethylene," *J. Phys. Chem.*, 75(1971)613-616.
- Kazanjian, A. R. and M. E. Killion, Results of experiments on radiolytic gas generation from sludge, Rockwell International, Rocky Flats Plant, personal communication reference in Tru-PACT Safety Analysis Report, 1981.
- Kazanjian, A. R. "Radiolytic Gas Generation in Plutonium Contaminated Waste Materials," Rockwell International, Rocky Flats Plant, RFP-2469, October 1976.
- Kosiewicz, S. T. "Gas Generation from the Alpha Radiolysis of Bitumen," *Nuclear and Chemical Waste Management*, 1(1980)139-141.
- Kosiewicz, S. T. "Gas Generation from the Organic Transuranic Wastes. I. Alpha Radiolysis at Atmospheric Pressure," *Nuclear Technology*, 54(1981)92-99.
- Kosiewicz, S. T. et al., "Studies of Transuranic Waste Storage Under Conditions Expected in the Waste Isolation Pilot Plant (WIPP), Interim Summary Report October 1, 1977-June 15, 1979," Los Alamos National Laboratory, LA-7931-PR.
- Krasnansky, V. J. et al., "Effect of Gamma Radiation on Chemical Structure of Plastics," *SPE (Society of Plastics Eng.) Trans.*, 1(1961)133-138.
- Ladrielle, et al., "Alpha and Gamma Induced Radiolysis of Tributyl-Phosphate," *Radiochem. Radioanal. Letters*, 59(1983)355-364.
- Le Chevallier, M. W., C. D. Caethon, and R. G. Lee, "Factors promoting survival of bacteria in chlorinated water supplies," *Appl. Environ. Microbiol.*, 54:649(1988).
- Lewis, E. L. "TRU Waste Certification: Experimental Data and Results," Monsanto Research Corp., Mound Laboratory, MLM-3096, Sept. 1983.
- Liverhant, S. E., "Elementary Introduction to Nuclear Reactor Physics," John Wiley & Sons, New York, 1960.
- Ludowise, J. D. "Report on Plutonium Mining Activities at 216-Z-9 Enclosed Trench," Rockwell International, Rockwell Hanford Operations, RHO-ST-21, September 1978.
- Makhlis, F. A. *Radiation Physics and Chemistry of Polymers*, John Wiley & Sons, New York, 1975, translated from the Russian.
- Mandelkern, L. "Radiation Chemistry of Linear Polyethylene," in *Radiation Chemistry of Macromolecules*, Vol. I, ed. M. Dole, Academic Press, New York, 1972.

7. References

- Parker Seals, Parker O-Ring Handbook, Lexington, KY, 1992.
- Parkinson, W. W. and R. M. Keyser, "Radiation Chemistry of Substituted Vinyl Polymers. Polystyrene and Related Polymers," in *The Radiation Chemistry of Macromolecules*, Vol. II, ed. M. Dole, Academic Press, New York, 1973.
- Pillay, K. K. S., "The Effects of Ionizing Radiation on Synthetic Organic Ion Exchangers," *J. Radioanal. Nuc. Chem.*, 97/1(1986)135-210.
- Rowbottom, R. S., "Risks of Bacterial Hydrogen Generation in White Water Systems," *Tappi Journal*, 76:1(1993)97-98.
- Schnabel, W., *Polymer Degradation—Principles and Practical Applications*, Macmillan Publishing Company, Inc., New York, 1981.
- Smith, J. M., *Chemical Engineering Kinetics*, McGraw-Hill Book Co., New York, 1981.
- Sobashima, S. et al., "Irradiation Effects on Polyoxymethylene," in *Annual Report on the Japanese Assn. for Radiation Research on Polymers*, AEC-tr-6231, 1(1959)329-338.
- Spinks, J. W. T. and R. J. Woods, *An Introduction to Radiation Chemistry*, John Wiley & Sons, New York 1976.
- Sullivan, J. C. "Reactions of Plutonium Ions with the Products of Water Radiolysis," in *Plutonium Chemistry*, W.T. Carnal (Ed.), American Chem. Soc. ACS Symp., 216(1983)241.
- Szymanski, W. et al., "Increase of Poly (Vinyl Chloride) Stability Towards Ionizing Radiation. II. Effects of Epoxidic Addition in PVC Films. III. Effects of the Addition of Ethylene Glycol Bis- beta- Aminocrotonate in PVC Foils," *Nukleonika*, 21(1976)277-283.
- Turner, D. T., "Radiation Chemistry of Some Miscellaneous Polymers. Polyethylene Terephthalate," *The Radiation Chemistry of Macromolecules*, Vol. II, ed. M. Dole, Academic Press, New York, 1973.
- U. S. Department of Energy, "Radioactive Waste Management," DOE Order 5820.2A, September 26, 1988.
- U. S. Environmental Protection Agency, "Environmental Standards for the Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Waste, Final Rule," 40 CFR Part 191, Federal Register, Vol. 50, No. 182, 1985.
- Van der Kooij, D., A. Visser, and W. A. M. Hijnen, "Determining the concentration of easily assimilable organic carbon in drinking water," *J. Amer. Water Works Assoc.*, 74:540(1982).
- VanDevender, W. H., "Slatec Mathematical Subprogram Library Version 2.0," Sandia National Laboratories, SAND84-0281, April 1984.
- Varsanyi, "Investigations into the Permeability of Polymer Membranes of Food Packaging quality to Gases and Water Vapor after Radiation Treatments with Radurizing Doses," *Acta Alimentaria*, 4(1975)169-251.
- Wang, R., F.P. Healey, and J. Meyers, "Amperometric measurement of hydrogen evolution in *Chlamydomonas*," *Plant Physiol.*, 48(1971)108-110.
- Weast, R. C., ed., *CRC Handbook of Chemistry and Physics*, CRC Press, Inc., Boca Raton, FL, 1979.
- Wetzel, R. G. and B. A. Manny, "Decomposition of Dissolved Organic Carbon and Nitrogen Compounds from Leaves in an Experimental Hard-Water Stream," *Limnol. Oceanogr.*, 17:927(1972).

APPENDIX A. CHEMICAL REACTIONS

Many chemical reactions that produce hydrogen gas involve a change in the valance of metal atoms or ions and the formation of hydrogen from the combination of hydrogen ions or from the dissociation of water. Additionally, hydrogen is produced when a metal hydride is converted to a metal oxide or to a metal hydroxide by reaction with oxygen-containing species, such as hydroxide ions, oxygen, or water.

Metals that are more electropositive than hydrogen (above hydrogen in the electromotive force series) will liberate hydrogen gas upon reaction with dilute acid solutions or in some cases water. These metals include: Sn, Ni, Ti, Cd, Fe, Zn, Al, Be, Mg, Na, Ca, Sr, Ba, Rb, K, and Li.

Example reactions between hydrogen ions and metals include:



The reaction between metallic sodium and water is:



Calcium hydride will also react with water to give hydrogen gas:



The dissolution of aluminum or silicon in alkali solution produces hydrogen according to the reactions:



Corrosion of metal comprising the packaging (including inner containers) is a phenomenon which can appear either generalized or local. Corrosion depends on the following parameters: (1) type of metal or alloy, (2) chemical properties of the surrounding water or vapor (pH, oxidant concentration, etc.), and (3) temperature and pressure of the surrounding medium. In addition to influencing the corrosion rate, these parameters affect the type and quantity of the corrosion products.

The following mechanisms describe the corrosion reaction between iron and water:



These two reactions will dominate over other iron corrosion reactions if the medium surrounding the wastes is anaerobic. If no consideration is given to consumption of hydrogen after its formation, then the volume of hydrogen produced will be directly related to the quantity of iron corroded.

In complex mixtures of transuranic isotopes, water, inorganics, and organics (e.g., lubricants, oils, solvents, resins), predicting all possible reactions that lead to hydrogen evolution may be difficult even if all the mixture constituents are known. In some radioactive liquid and sludge wastes, the hydrogen (and other flammable gas) generation rate has been found to be greater than that predicted from radiolysis (McDuffie 1994; Hopkins 1994). The discrepancy has been attributed to hydrogen produced by chemical

R is the gas law constant [8.314 J/mol·K]; and

T is the reaction temperature [K].

Although 10 CFR 71.43(d) requires that a package be made of materials and construction that assures that there will be no significant chemical, galvanic, or other reaction among the packaging components, among package contents, or between the packaging components and the package contents, for certain contents such as non-solidified radioactive liquid and sludge waste mixtures, there may be some hydrogen evolution due to chemical reactions among the constituents in the contents. For waste mixtures where the chemical generation of hydrogen is unavoidable, the appropriate activation energy and waste temperature should be used to estimate the rate of hydrogen evolution.

of thermal tests (in the absence of experimental data) on the polymeric materials by subjecting them to simulated transport conditions to determine the generation rate of hydrogen (and other flammable gases) and any potentially corrosive products may be necessary. When a transportation package contains a mixture of polymeric materials, experimental data concerning the thermal degradation of individual polymeric materials should be used with caution since it has been demonstrated that mixtures of polymers can have different (larger) thermally generated amounts of gases than the simple sum of the individual polymer contributions.

Some experimental results of polymer degradation studies for selected polymers are presented in Table B.3. From Table B.3, it is clear that significant thermal degradation should be expected for many polymers if the temperature is greater than about 473 K (392°F). However, for essentially all TRU waste transportation containers, the waste does not experience temperatures greater than about 393 K (248°F) as a result of the relatively low decay heats. Although most polymeric materials will not undergo significant thermal degradation at a temperature of 393 K (248°F), this temperature is above the maximum continuous service temperature (MCST) for some polymeric materials and a limited amount of thermal degradation may be expected to occur. The MCST is based on the polymer maintaining its required structural properties. Above the MCST, the material could be expected to soften (except for thermosetting resins) as it approaches its glass transition temperature and may release some trapped solvents, plasticizers, and other low-volatility materials and may also undergo some limited thermal degradation. Based on a maximum contents temperature of about 393 K (248°F), the polymers typically in TRU waste that should be examined as to their thermal degradation gas emission rate include (but are not limited to) nylon, polyethylene, polystyrene, polyvinylchloride, and epoxy.

Thermal degradation experiments performed on some common waste materials (such as cellulose, plastics, and rubbers) at temperatures as high as 373 K (212°F) indicate that the moles of gas generated per kilogram of material would be 1.23×10^{-3} moles/kg (2.7×10^{-3} moles/lbm) waste material (Kosiewicz 1979). In addition, carbon dioxide and carbon monoxide are the common thermal degradation products and, although these gases would contribute to the total containment vessel gas pressure, they would not contribute to the inventory of flammable gases.

A second-order effect that may be important to consider is the release of HCl from the thermal degradation of polyvinylchloride. It is possible that thermally liberated hydrogen ions could undergo corrosion reactions with metals present, which would result in a release of hydrogen gas as a corrosion product.

Table B.1 Vacuum Outgassing of Some Common Polymers at 298 K (Parker Seals 1992)

Polymer	Compound #	% Wgt. Loss	Polymer	Compound #	% Wgt. Loss
Butyl	B612-70	0.18	Nitrile	N674-70	1.06
Neoprene	C873-70	0.13	Polyurethane	P648-90	0.129
Ethylene Propylene	E515-80	0.39	Silicone	S455-70	0.03
Ethylene Propylene	E529-60	0.92	Silicone	S604-70	0.31
Ethylene Propylene	E692-75	0.76	Fluorocarbon	V747-75	0.09
Fluorosilicone	L449-65	0.28	Fluorocarbon	V884-75	0.07
Fluorosilicone	L677-70	0.25	Fluorocarbon	V894-90	0.07
Nitrile	N406-60	3.45			

Table B.3 Various Thermal Degradation Results for Polymers

Compound	Experimental Results	References
Polystyrene	When polystyrene is subject to temperatures in the range of 633-693 K (680-788°F), many volatile flammable products are released, including benzene, toluene, ethylbenzene, and diphenylpropanes.	Carniti 1991
Polypropylene (filled)	When filled polypropylene (Taboren) was heated for 35 minutes at 533 K (500°F), many low molecular weight volatile products were released, including methane, ethane, ethene, propene, butene, 1,3-butadiene, acetone, pentane, etc.	Pacakova and Leclercq 1991
Polyethylene	Thermal oxidation of polyethylene shows gradual energy absorption until melting at about 383 K (230°F), and then combustion occurs at about 523 K (482°F). Polyethylene will release only minimum amounts of toxic or flammable gases at 343 K (158°F). Under air at 773 K (932°F) in flameless conditions, compounds typical of the thermal degradation of polyethylene included: 1-alkenes (present in the largest amounts), and the corresponding α,ω -alkadienes and n-alkanes. The only other substance present was triethylphenol.	Pacakova and Leclercq 1991
Polyethylene-Coated Paper	When subject to a flameless temperature of 773 K (932°F) in air, polyethylene-coated paper released acetone alcohol, trimethoxymethane, and other higher molecular weight substances.	Pacakova and Leclercq 1991
Milk Package	When the milk package material was subject to 773 K (932°F) air in flameless conditions, the characteristic products of burning polyethylene were formed, i.e. the 1-alkenes, α,ω -alkadienes and n-alkanes. In addition, the corresponding alkylaldehydes and derivatives of furals were present.	Pacakova and Leclercq 1991
Polyamide 6	The experimentally obtained thermogravimetric curve for polyamide 6, when heated at a rate of 2 K/min under helium, shows that significant volatile products are released when the temperature reaches about 553 K (536°F) and that the highest release rate of volatile products occurs when the temperature is about 688 K (779°F). Although the polymer decomposes quantitatively producing a high amount of the monomer ϵ -caprolactame ($\geq 90\%$), a significant amount of volatile materials are released with molecular weights between 15 and 30. For decomposition of a 2×10^{-5} kg (4.4×10^{-5} lbm) sample, the apparent activation energy was about 200 kJ/mole, the pre-exponential factor was $\log_{10}(A)=14.2$, and the calculated apparent reaction order was 0.82. For this material, there was no effect on the apparent activation energy due to the initial sample size.	Bockhorn 1996

APPENDIX C. BIOLOGICAL ACTIVITY

Biological activity within TRU waste can be a source of gas generation. Although most TRU wastes lack sufficient substrate to support biological growth and do not provide an environment conducive to biological activity, some wastes that contain soils or other potentially biologically contaminated materials need to be evaluated for their potential to generate gases. The primary concern is the possible release of gases from biological systems within the waste that may cause an increase in containment vessel flammable gas concentration.

Growth of biological systems results when viable organisms utilize nutrients in the medium in which they are contained to sustain growth (Characklis 1988). Not all organic compounds are equally susceptible to microbial decomposition; the fraction that provides energy and carbon for bacterial growth has been called labile dissolved organic carbon (Wetzel and Manny 1972; Ogura 1975), biodegradable organic carbon (Joret et al. 1988), or assimilable organic carbon (Van der Kooij et al. 1982). Some forms of TRU waste and many of the packaging materials inside the containment vessel (plastics) are organic materials. The potential for microbial activity may exist if there is a suitable environment for the degradation of the organic substrates. Factors other than nutrients that influence growth or regrowth of bacteria in transportation packages include temperature (Fransolet et al. 1985), residence time in packaging (Maul 1985), and the efficacy of disinfecting techniques (Le Chevallier et al. 1988).

Many types of microorganisms should be considered in the degradation of TRU waste. Aerobic microorganisms, which produce carbon dioxide and water, require oxygen for growth. Aerobic organisms do not generate any flammable gases; any increase in pressure due to the carbon dioxide and water generated is somewhat offset by the oxygen consumed, especially if the conditions permit condensation of the water vapor. Anaerobic microorganisms, which can produce carbon dioxide, hydrogen, methane, and other products, degrade materials in oxygen-free environments (Hartel and Buckel 1996; Wang et al. 1971; Rowbottom 1993; Nakamura et al 1993; Kalia and Joshi 1995). Anaerobic microorganisms include facultative anaerobics, which can live with or without oxygen, and obligate anaerobics, which cannot tolerate any oxygen. Microorganisms most likely to be found in TRU waste products include bacteria and fungi. Bacteria utilize only the surface of the materials, whereas fungi can access the matrix of the material and are generally found in aerobic environments.

Of the various waste forms in TRU waste, only cellulosic materials are generally important in terms of the potential for gas generation via biological-induced degradation. Rubber or plastic materials are more resistant to microbial actions. The contribution of these compounds to the total gas generation will be negligible because of their inert nature. Sampling programs, where drums of TRU waste (in retrievable storage up to 15 years) were opened and examined for degradation, found little or no degradation of the packaging materials (NRC Docket No. 71-9218, Aug. 11, 1999). Even under conditions designed to promote microbial proliferation, rubber and plastic degrade very slowly, if at all. Similarly, solidified inorganic sludges, which have high alkalinity (pH=10–12) that is hostile for most common microorganisms, should not exhibit any significant microbial gas generation.

Examples of cellulosic materials that could be present in TRU waste are cotton and paper products. Biodegradation of cellulose, which is a polymer composed of chains of glucose monomers, requires hydrolysis of the polymer into monomer units. Biological depolymerization is a slow process. Wood is also present in TRU waste, but degrades at a much slower rate than cellulose alone because of the microbial-resistance of the lignin in wood. Since bacterial action is a strong function of surface area and substrate availability, TRU waste is typically not very conducive to high microbial activity as a result of

APPENDIX D. RADIOLYTIC G-VALUES FOR VARIOUS MATERIALS

D.1 Radiolysis of Water

The radiolysis of water has been studied more than that of any other compound. Using pulse radiolysis techniques, it has been shown (Sullivan 1983) that the primary decomposition products of pure water about 10^{-9} seconds after the irradiation pulse from a ^{60}Co gamma source are: $\text{H}_2\text{O} \rightarrow \text{H}^+_{\text{aq}}, \text{OH}^-, \text{e}^-_{\text{aq}}, \text{H}, \text{H}_2\text{O}_2, \text{H}_2$, and OH^\cdot . The amounts of these products per 100 eV absorbed (G_R values) are respectively 2.9, 2.75, 2.65, 0.65, 0.70, 0.45, and 0.25. Many of the water radiolysis decomposition products are reactive radicals and excited species (e.g., e^-_{aq} is a strong reducing agent, and OH^\cdot is a strong oxidizing agent) that undergo further reaction with each other and with the water molecules to give the final products. The G values may vary slightly with energy and type of irradiation particle over a wide range of particles and energies (Sullivan 1983).

Experimental results for the radiolysis of water at room temperature show that $G(\text{H}_2)$ for water varies from 0.4 to 1.7 and that the bounding $G(\text{H}_2)$ for water subject to alpha radiation is 1.6. Representative results from studies on hydrogen generation from the radiolysis of water at room temperature are presented in Table D.1.

D.2 Radiolysis of Unsubstituted Hydrocarbons

D.2.1 Saturated Hydrocarbons

Saturated hydrocarbons contain only hydrogen and carbon atoms and single carbon-carbon bonds. As a group, saturated hydrocarbons include most common petroleum fuels, such as methane, propane, and octane. From experimental results on the radiolysis of saturated hydrocarbons, the bounding $G(\text{H}_2)$ value is 5.6 for saturated hydrocarbons in the liquid phase at room temperature in which the activity is due to alpha decay. Table D.2 lists experimental G values for saturated hydrocarbons irradiated at room temperature in vacuum. The radiolytic G values presented include $G(\text{H}_2)$, $G(\text{CH}_4)$, and $G(\text{gas})$.

Some general observations have been noted concerning the radiolytic products from saturated hydrocarbons (Newton 1963). Normal saturated hydrocarbons yield principally hydrogen, with methane being produced only from the methyl end groups. Therefore, for normal hydrocarbons, the ratio of hydrogen to methane increases with increasing molecular weight. With branched-chain hydrocarbons, relatively more methane is produced, and the yield of methane increases with the number of methyl groups on the hydrocarbon chain. An activation energy for the $G(\text{H}_2)$ value for radiolysis of liquid neopentane and n-hexane, which is the energy required to initiate the reaction and is useful for calculating the temperature-dependence of the G -value, was measured to be approximately 3 kcal/mole (Hall 1963).

D.2.2 Unsaturated Hydrocarbons

Unsaturated hydrocarbons are hydrocarbons that have at least one double or triple carbon-carbon bond. Examples include acetylene, ethylene, 1-hexene, and cyclohexene. In general, for a given number of carbon atoms, unsaturated hydrocarbons exhibit lower radiolytic G -values than the corresponding saturated hydrocarbons. Table D.3 lists radiolytic G values for several unsaturated hydrocarbons irradiated in vacuum at room temperature.

D.3.4 Carboxylic Acids

Carboxylic acids contain the carboxyl group attached to either an alkyl group (RCOOH) or an aryl group (ArCOOH), with respective structures:



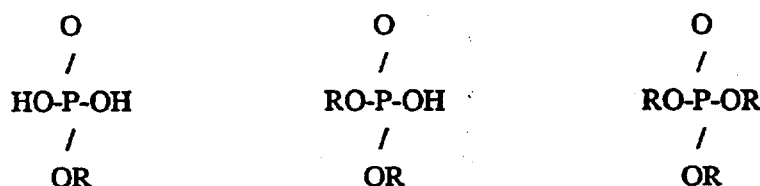
Table D.5 lists experimental radiolytic G values for two carboxylic acids that are liquids at room temperature.

D.3.5 Esters

Esters are functional derivatives of carboxylic acids in which the -OH of the carboxyl group is replaced by -OR'. (Phosphate esters are discussed separately.) The emulsifier for Envirostone, a gypsum-based material used to solidify organic and low pH aqueous sludges and liquid waste, has been identified as a polyethyl glycol ester. In addition, many plasticizers added to polymers to form commercial plastics are esters. Table D.5 presents experimental G-values for many esters. Benzyl acetate contains a benzene ring and has a much lower G(H₂) value than the other esters.

D.3.6 Phosphate Esters

Phosphate esters have one of the following structures (Morrison and Boyd 1973):



Tricresyl phosphate contains three benzene rings and has a much lower G(H₂) value than either trioctyl or tributyl phosphate.

Tri-n-butyl phosphate (TBP), an organic ester of phosphoric acid, is used as an extractant in the reprocessing of nuclear fuel. Radiolysis experiments have been conducted to determine the decomposition products of TBP in different phases of the extraction system. The purex process uses a solution of TBP in dodecane (Ladrielle et al. 1983). Experiments were conducted using both gamma and alpha radiolysis of TBP and solutions of TBP in dodecane. The average alpha particle energy used in the radiolysis experiments was estimated to be 10.5 MeV (alpha particles from a cyclotron). Radiolysis of pure TBP resulted in the formation of mono and dibutylphosphate, butanol, and saturated hydrocarbons (hydrocarbon chains from 5 to 11 carbon atoms long). Radiolysis of pure decane yielded saturated hydrocarbons. Holland (1978) performed gamma radiolysis experiments on TBP, dodecane, and mixtures of TBP and dodecane. The values of G(H₂)=6.7 and G(CH₄)=0.05 were determined for dodecane. Corresponding G values for pure TBP were G(H₂)=2.0 and G(CH₄)=0.3. Radiolysis of mixtures of TBP and dodecane were found to yield less hydrogen than would be predicted by the mixture law, but the yield of acid was greater than that predicted by the mixture law.

Aromatic hydrocarbons, such as benzene, toluene, and cyclohexene protect TBP from radiolysis, while saturated hydrocarbons such as hexane, cyclohexane, and dodecane sensitize TBP to radiolytic degradation (Barney and Bouse 1977). Carbon tetrachloride has also been found to sensitize TBP

the Rocky Flats Plant; (2) vacuum pump oil (DuoSeal); and (3) Rykon lubricating grease. A summary of the results of these radiolysis studies is provided in Table D.8.

D.7 Radiolysis of Polymers

Polymers, including polyethylene, PVC, and cellulose, are common organic solids found in TRU wastes. Other solids, such as solidified organic liquids, aqueous sludges, and bitumen are discussed in Section D.8. The controlling factor in the behavior of polymers under irradiation, as under most other environmental influences, is the chemical structure. This section provides both general information concerning the relative radiation resistance of polymers and experimental radiolysis results on various polymers. Generalized reasonable bounding values are then determined for classes of polymers based on functional groups.

Radiolysis of polymers generally results in two types of reactions: chain scission and crosslinking. Chain scission (degradation) is the term used for breaking of main-chain bonds in polymer molecules, which results in the formation of species of lower molecular weight. When scission of the polymer is predominate, structural strength and plasticity are rapidly lost. The polymer may eventually crumble to a powder. Crosslinking results in insoluble and infusible network structures because of increased molecular weight and size. Generally, competition occurs between the two reaction mechanisms.

Additives can be used to improve the aging properties of polymers subject to radiation. Commercial plastics and paper contain additives that modify the properties of the base polymer in the material. The additives generally improve the radiation stability of the commercial materials and reduce G values for flammable gases. Organic additives can be subdivided into two categories: energy-sink materials, and chemical reactants. Energy sink materials are characterized by having aromatic characteristics and correspondingly low G values.

In the absence of oxygen, polymers can be divided into classes according to their tendency to degrade or crosslink. Polymers that predominantly crosslink when exposed to radiation have the following radiation resistance according to their functional groups and structure: aromatic > unsaturated > saturated. The radiation resistance of polymers that are borderline between crosslinking and scission generally follows: S-in main chain > aromatic > ester > halogen > saturated. For polymer that predominantly scission when exposed to radiation the radiation resistance ordering is: aromatic > ester > alcohol > halogen > saturated. Oxygen enhances the degradation of most polymers. Table D.9 summarizes some common polymers in order of their decreasing resistance when irradiated to net molecular-weight change for polymers that predominantly crosslink, are borderline between crosslinking and scission, or that predominantly undergo scission.

Polymers that are less radiation resistant tend to generate more flammable gas from radiolysis. Materials that have relatively high radiolytically-generated flammable gas production rates (i.e., $G(\text{flam gas})=5-7$) include saturated hydrocarbons and polymers containing alcohol or ether functional groups. Materials that have moderate radiolytically-generated flammable gas production rates (i.e., $G(\text{flam gas})=2-3$) include unsaturated hydrocarbons and polymers containing ester functional groups. Materials that have relatively low radiolytically-generated flammable gas production rates (i.e., $G(\text{flam gas}) < 1$) include polymers with aromatic characteristics. A summary of the influence of chemical structure on flammable gas production rates is given in Table D.10. A summary of the maximum G values observed for polymers containing only carbon, hydrogen, nitrogen, oxygen and halogens are listed in Table D.11. Relative G(gas) values for some miscellaneous commercial plastics are presented in Table D.12.

D.7.6 Cellulose

TRU waste may contain many different types of cellulose such as cotton cellulose, sulfite cellulose, wood cellulose, and they may have a wide range of crystallinity. In addition, many materials are made of or contain cellulose, such as paper, cloth, wood, Benelex, cellophane, cellulose acetate (rayon, molded items, paints, coatings), and ethyl cellulose (paints, molded items). Radiolysis experiments have been performed on many types of cellulose and on the various cellulose-containing products using gamma radiation, electrons, and alpha particles (Kosiewicz 1981; Zerwekh 1979; Ershov et al. 1986; Arthur 1970; Dalton et al. 1963). Based on the available experimental data, extremely conservative bounding G values for cellulose and cellulose products are estimated to be $G(H_2)=3.2$, $G(\text{flam gas})=3.2$, and $G(\text{gas})=10.2$. If sulfite cellulose and cotton cellulose are not present in the waste, reasonable bounding G values are estimated as $G(H_2)=1.4$ and $G(\text{flam gas})=1.4$, and $G(\text{net gas})=6.2$.

D.7.7 Urea-Formaldehyde

Urea-formaldehyde is a possible solidification medium for nuclear power reactor wastes. Although strongly dose dependent, the G values for doses corresponding to those seen in TRU waste packages during transportation are $G(H_2)=2.4$, $G(\text{flam gas})=2.4$, and $G(\text{net gas})=2.8$.

D.7.8 Polyoxymethylene

A few authors have reported radiolysis results for polyoxymethylene (Krasnansky et al. 1961; Dole 1973; Sobashima et al. 1959; Nitta 1961). The radiolysis gases typically included about 15% H_2 , 67% CO_2 , 1% CO, 10% CH_4 , 1% methyl formate, 2% methyl ether, and 3% other gases (all volume percent). At room temperature, the bounding radiolytic G values are estimated as $G(H_2)=2.1$, $G(\text{flam gas})=5.6$, and $G(\text{net gas})=14.1$.

D.7.9 Polypropylene Oxide

It has been determined (Geymer 1973) that polypropylene oxide is more susceptible to degradation under irradiation than polypropylene, and yields less hydrogen. The bounding G values for polypropylene oxide are $G(H_2)=1.0$, $G(\text{flam gas})=1.1$, and $G(\text{net gas})\leq 1.4$. the bounding G values for polypropylene are $G(H_2)=1.1$, $G(\text{flam gas})=1.2$, and $G(\text{net gas})\leq 1.6$.

D.7.10 Polyvinyl Formal

From irradiation experiments in a graphite reactor, the $G(\text{gas})$ value for polyvinyl formal was found to be 1.4 times the value measured for polyethylene (NRC Docket No. 71-9218, Aug. 11, 1999).

D.7.11 Polybutadiene and Polyisoprene

Latex is the commercial name for polybutadiene and polyisoprene. The bounding G vales for Latex are estimated as $G(H_2)=0.7$, $G(\text{flam gas})=0.9$ and $G(\text{net gas})=0.9$ (Kazanjan 1976; Zerwekh 1979; Bohm 1973).

D.7.12 Polymethyl Methacrylate (PMMA)

The main volatile products from the alpha radiolysis of PMMA are H_2 , CO_2 , CO, CH_4 , propane and methyl methacrylate monomer (Kazanjan 1976; Zerwekh 1979; Chapiro 1962; Busfield et al. 1982; Bolt and Carroll 1963). Reasonable bounding G values for the radiolysis of PMMA are estimated as $G(H_2)=0.4$, $G(\text{flam gas})=2.0$, and $G(\text{net gas})=4.1$.

D.7.19 Polychloroprene

Neoprene rubber is composed of polychloroprene. Many gamma-radiolysis results of polychloroprene have been reported in the literature. The main gaseous products from the radiolysis of polychloroprene are H_2 , HCl , CO , CO_2 , and other miscellaneous short-chain hydrocarbons. The bounding radiolytic G values are estimated as $G(H_2)=G(\text{flam gas})=0.1$ and $G(\text{net gas})=0.7$. The reasonable bounding $G(HCl)$ for the radiolysis of polychloroprene is estimated as 0.06.

D.7.20 Chlorosulfonated Polyethylene

Hapalon ® gloves are composed of chlorosulfonated polyethylene. In addition lead oxide is often incorporated into the gloves to provide gamma shielding. Radiolysis experiments on commercial Hapalon ® indicate that the bounding G values are $G(H_2)=G(\text{flam gas})=0.3$ and $G(\text{net gas})=0.6$ (Koslewicz 1981; Kazanjian 1976; Zerwekh 1979; Arakawa 1986).

D.7.21 Polytetrafluoroethylene (PTFE) and Polychlorotrifluoroethylene

Since both Polytetrafluoroethylene and Polychlorotrifluoroethylene contain no hydrogen in their base polymers, $G(H_2)$ and $G(\text{flam gas})$ for these materials is zero. Almost all the radiolysis gases produced by these compounds is CO_2 . The bounding $G(\text{net gas})$ value found was 1.1 (NRC Docket No. 71-9218, Aug. 11, 1999).

D.7.22 Polyamides

Polyamides are a class of compounds that include such commercial products as Nylon and Nomex. G values for polyamides can be bounded with $G(H_2)=1.1$, $G(\text{flam gas})=1.2$, and $G(\text{net gas})=1.5$ (Krasnansky et al. 1961; Dole 1983; Zimmerman 1973).

D.7.23 Ion-Exchange Resins

The G values for synthetic organic resins, which comprise the vast majority of ion-exchange resins, depend on the resin and the ionic form of the resin (Pillay 1986). Of the many ion-exchange resins investigated, the bounding G values were found to be $G(H_2)=G(\text{flam gas})=1.7$ and $G(\text{net gas})=2.1$. Most G values for ion-exchange resins were much lower than the bounding values indicated. If an ion-exchange resin is to compose a major portion of a waste shipment, determining the relevant G values for that particular material may be useful.

D.8 Radiolysis of Non-Polymer Solids

Non-polymer solids include solidified liquid wastes, solid organic acids, asphalt, and miscellaneous inorganic solids.

D.8.1 Radiolysis of Solidified Liquid Wastes

Solidified liquid wastes include sludges, concretes, and gel-like or monolithic structures that bond liquid wastes so that free liquids are minimized.

D.8.1.1 Aqueous Sludges

Radiolysis experiments have been conducted (Kazanjian and Killion 1981) on a common sludge produced at the Rocky Flats Plant to determine the radiolytic gas yields as a function of water content and nitrate content. This sludge was produced by the neutralization of nitric acid solutions in the

Table D.1 Radiolytic $G(H_2)$ Values for Water at 298 K

Phase	$G(H_2)$	Comments	References
gas	0.5	gamma, electron	Spinks and Woods 1976
liquid	0.4	gamma, electron, pH=0.5	Spinks and Woods 1976; Burns and Sims 1981
liquid	0.45	gamma, electron, pH=3-13	Spinks and Woods 1976; Burns and Sims 1981
liquid	1.1	6.4 MeV He ⁺⁺	Burns and Sims 1981
liquid	1.3	Cm-244 alpha (5.8 MeV)	Bibler 1974
liquid	1.6	5.3 MeV alpha (Po), pH=0.5	Spinks and Woods 1976
liquid	1.7	Cf-252 alpha, beta, fission frags, 0.4M H ₂ SO ₄	Bibler 1975

dose rates, the $G(H_2)$ values reported were 4.5 for octane and 2.0 for vacuum pump oil. The radiolysis gases were predominantly hydrogen and had the nominal ratio $H_2/CO_2/CH_4 = 1.0/0.03/0.01$.

Studies of water adsorbed onto inorganic oxides (SiO_2 , SiO_2-Al , SiO_2-Ca , Er_2O_3 , La_2O_3 , and Al_2O_3) subject to gamma radiation indicate that energy transfer can occur from the oxide to the water molecules (Garibov 1983). Values of $G(H_2)$ measure indicate that the energy transferred from the oxide to the absorbed water can be 3-5 times the energy originally absorbed by the water (based on its mass fraction). For water-inorganic oxide systems, an increase in temperature led to a decrease in $G(H_2)$, which was attributed to a greater desorption rate of water molecules from the oxide surface at the higher temperatures and the corresponding decrease in effective energy transfer from the oxide to the absorbed water molecules.

D.8.2 Radiolysis of Solid Organic Acids

$G(H_2)$ values for some organic acids that are solid at room temperature have been reported in the range from 1.2 to 2.3 (Bolt and Carroll 1963). $G(gas)$ values for the same materials range from 1.8 to 4.1. The maximum G value for flammable gas was 2.6. A value of $G(CO_2)$ of 14 has been reported for one of the organic acids (isobutyric acid) (Spinks and Woods 1976):

D.8.3 Radiolysis of Asphalt

A value of $G(gas)$ for bitumen (asphalt) for low absorbed dose was estimated to be 1.3, with hydrogen being the primary gas evolved (Kosiewicz 1980). No dependence on temperature was observed from 20 to 70°C. Gamma radiolysis experiments reported by Burnay (1987) measured lower G values.

D.8.4 Radiolysis of Soil

Gas evolved from plutonium-contaminated soil has been reported (Pajunen 1977). The soil was removed from the Z-9 trench at the Hanford site, which had been used as a liquid waste disposal site for the Plutonium Finishing Plant. The waste solutions deposited in the trench were acidic and consisted of (1) aluminum, magnesium, calcium, and other metal nitrate salt wastes, (2) degraded solvents (15% tributyl phosphate or dibutyl phosphate in CCl_4), and (3) other organics, such as solvent washings, fabrication oil, and other waste materials from hood and equipment flushings (Ludowise 1978). The top 30 cm of soil was sampled from the trench. The soil moisture content ranged between 0.2 and 25.5 wt. %, averaging approximately 5 wt. %. Organic content averaged 7.1 wt. % with a range of 0.2 to 46.4 wt. %. The highest value of $G(gas)$ calculated from Pajunen's data was 1.6, for a soil having a combined organic and moisture content of about 15 wt. %. The typical composition of the gas generated by the soils was 50% N_2 , 14% O_2 , 23% H_2 , and 13% CO_2 (percents for gases are volumetric).

Soil samples from Mound Laboratory property were contaminated with plutonium dioxide (particles averaging ~ 20 μm) and analyzed for radiolytic gas generation. Gas generation was measured from a soil sample that contained about 5 wt. % water. The $G(gas)$ value was 0.22, with $G(H_2)=0.15$ and $G(CO_2)=0.07$. Oxygen was consumed, with $G(-O_2)=0.10$ (NRC Docket No. 71-9218, Aug. 11, 1999).

D.8.5 Radiolysis of Dry, Solid Inorganic Materials

Dry, solid inorganic materials do not generate hydrogen but may produce other gases (frequently oxygen).

Some common inorganic chemicals used in processing aqueous wastes include ferric sulfate, calcium chloride, and magnesium sulfate. A treatment process has been identified (Kazanjan and Killion 1981)

that produces a precipitate of hydrated oxides of iron, magnesium, aluminum, silicon, etc. In addition, various nitrates and carbonates can be present in dry solid inorganic materials.

For stoichiometric decomposition of nitrates, a value of $G(O_2)$ should be one-half of the $G(NO_2^-)$ value. A value of $G(O_2) < 1.3$ has been determined (Johnson 1970). G values measured for gamma radiolysis of barium, potassium, and sodium chlorates had $G(Cl^-) < 1.8$ and $G(O_2) < 4.0$.

For alkali and alkaline earth perchlorates, values of $G(Cl^-) < 1.1$ and $G(O_2) < 5.3$ were measured. Neither ozone nor free chlorine were detected in radiolytic gas generation measurements on dry solid inorganic materials.

D.9 Radiolysis of Gases

Radiolysis of the nitrogen/oxygen mixture found in air produces a small amount of ozone, as well as oxides of nitrogen (Spinks and Woods 1976). In a closed system, back reactions lead to an equilibrium concentration of these gases of a few ppm for ozone to a few percent for NO_2 and N_2O . The NO yields are much smaller (Kazanjian and Brown 1969). When moisture is present, the main product is nitric acid, which is formed until the water vapor is exhausted (Spinks and Woods 1976; Kazanjian and Brown 1969). G values for nitric acid formation are about 1.0, but vary with water concentration (Kazanjian and Brown 1969).

Gaseous carbon dioxide is almost unaffected by ionizing radiation (Spinks and Woods 1976), possibly due to a back reaction between CO ozone to form CO_2 and O_2 .

Table D.1 Radiolytic $G(H_2)$ Values for Water at 298 K

Phase	$G(H_2)$	Comments	References
gas	0.5	gamma, electron	Spinks and Woods 1976
liquid	0.4	gamma, electron, pH=0.5	Spinks and Woods 1976; Burns and Sims 1981
liquid	0.45	gamma, electron, pH=3-13	Spinks and Woods 1976; Burns and Sims 1981
liquid	1.1	6.4 MeV He ⁺⁺	Burns and Sims 1981
liquid	1.3	Cm-244 alpha (5.8 MeV)	Bibler 1974
liquid	1.6	5.3 MeV alpha (Po), pH=0.5	Spinks and Woods 1976
liquid	1.7	Cf-252 alpha, beta, fission frags, 0.4M H ₂ SO ₄	Bibler 1975

Table D.2 Radiolytic G Values for Saturated Hydrocarbons at 298 K

Compound	Phase	G(H ₂)	G(CH ₄)	G(gas)	Experimental Conditions	References
propane	gas	8.2	0.4	NA	alpha, vacuum	Spinks and Woods 1976
n-butane	gas	9	1.2	NA	alpha, vacuum	Spinks and Woods 1976
isobutane	gas	7.4	2.7	NA	alpha, vacuum	Spinks and Woods 1976
pentane	gas	7.3	0.8	NA	alpha, vacuum	Spinks and Woods 1976
neopentane	gas	2	2	NA	alpha, vacuum	Spinks and Woods 1976
hexane	gas	5.6	0.8	NA	alpha, vacuum	Spinks and Woods 1976
pentane	liquid	4.2	0.4	NA	electron, vacuum	Spinks and Woods 1976
"	liquid	4.2	0.2	5.4	electron, vacuum	Hall 1963
hexane	liquid	5	0.2	5.2	electron, vacuum	Spinks and Woods 1976
"	liquid	5	0.1	7.2	electron, vacuum	Hall 1963
cyclohexane	liquid	5.6	0.1	5.7	electron, vacuum	Spinks and Woods 1976
"	liquid	5.3	0.0	5.3	alpha, vacuum	Spinks and Woods 1976
"	liquid	7.7	NA	NA	fission frags, vac.	Gaumann 1968??
heptane	liquid	4.7	0.1	NA	electron, vacuum	Spinks and Woods 1976
octane	liquid	4.8	0.1	NA	electron, vacuum	Spinks and Woods 1976
"	liquid	4.6	0.1	NA	gamma, air	Bibler and Orebaugh 1978
"	liquid	4.2	NA	NA	alpha, air	Bibler and Orebaugh 1978
nonane	liquid	5	0.1	NA	electron, vacuum	Spinks and Woods 1976; Bibler and Orebaugh 1978
decane	liquid	5.2	0.1	NA	electron, vacuum	Spinks and Woods 1976
docedane	liquid	4.9	0.1	NA	electron, vacuum	Spinks and Woods 1976
hexadecane	liquid	4.8	0.0	NA	electron, vacuum	Spinks and Woods 1976
2-methylpentane	liquid	4.0	0.5	NA	electron, vacuum	Spinks and Woods 1976
2,2-dimethyl-butane	liquid	2.0	1.2	NA	electron, vacuum	Spinks and Woods 1976
neopentane	liquid	1.6	3.7	5.6	gamma, vacuum	Hall 1963

Table D.3 Radiolytic G Values for Unsaturated Hydrocarbons at 298 K

Compound	Phase	G(H ₂)	G(CH ₄)	G(gas)	Experimental Conditions	References
ethylene	gas	1.2	0.1	2.8	electron, vacuum	Hall 1963
cyclohexene	liquid	1.3	0.0	1.3	gamma, vacuum	Spinks and Woods 1976
"	liquid	3.0	0.0	3.0	alpha, vacuum	Spinks and Woods 1976
1-hexene	liquid	0.8	0.0	0.8	electron, vacuum	Hall 1963

Table D.4 Radiolytic G Values for Common Aromatic Hydrocarbons at 298 K

Compound	Phase	G(H ₂)	G(CH ₄)	G(gas)	Experimental Conditions	References
benzene	liquid	0.6	0.0	0.8	alpha, vacuum	Spinks and Woods 1976
"	liquid	< 0.1	< 0.1	< 0.1	gamma, vacuum	Spinks and Woods 1976
"	liquid	< 0.1	< 0.1	< 0.1	electron, vacuum	IEEE S-146 1963
toluene	liquid	0.6	0.0	0.6	alpha, vacuum	Spinks and Woods 1976
"	liquid	0.1	< 0.1	0.1	gamma, vacuum	Spinks and Woods 1976
"	liquid	0.1	< 0.1	0.1	electron, vacuum	Hall 1963
p-xylene	liquid	0.2	0.0	0.2	gamma, vacuum	Spinks and Woods 1976
ethyl benzene	liquid	0.2	< 0.1	0.2	electron, vacuum	Hall 1963; IEEE S-146 1963
"	liquid	0.2	< 0.1	0.2	gamma, vacuum	Spinks and Woods 1976
"	liquid	0.2	< 0.1	0.2	reactor, vacuum	Hall 1963
isopropyl benzene	liquid	0.2	0.1	0.3	gamma, vacuum	Spinks and Woods 1976
"	liquid	0.2	0.1	0.3	electron, vacuum	Hall 1963; IEEE S-146 1963
"	liquid	0.3	0.1	0.4	alpha, vacuum	IEEE S-146 1963
"	liquid	0.2	0.1	0.3	reactor, vacuum	Hall 1963
tert-butyl benzene	liquid	0.1	0.1	0.2	electron, vacuum	Hall 1963; IEEE S-146 1963
"	liquid	0.2	< 0.1	0.2	reactor, vacuum	Hall 1963
mesitylene	liquid	0.2	< 0.1	0.2	electron, vacuum	Newton 1963
biphenyl	liquid	NA	NA	< 0.1	electron, vacuum	Hall 1963
"	liquid	NA	NA	0.1	reactor, vacuum	Hall 1963
p-terphenyl	liquid	< 0.1	< 0.1	< 0.1	electron, vacuum	Hall 1963
"	liquid	< 0.1	< 0.1	< 0.1	reactor, vacuum	Hall 1963

Table D.5a Radiolytic G Values for Various Oxygenated Compounds at 298 K

Compound	Phase	G(H ₂)	G(CO)	G(CH ₄)	G(gas)	Experimental Conditions	References
<i>Alcohols:</i>							
methanol	gas	10.8	1.0	0.3	12.1	gamma, vacuum	Spinks and Woods 1976
ethanol	gas	10.8	1.2	0.9	12.9	electron, vacuum	Spinks and Woods 1976
methanol	liquid	5.4	0.1	0.7	6.2	gamma, vacuum	Spinks and Woods 1976
"	liquid	3.5	0.2	0.4	4.5	alpha, vacuum	IEEE S-146 1963
"	liquid	4.0	0.2	0.2	4.4	gamma, vacuum	Hall 1963
ethanol	liquid	5.0	0.1	0.6	5.7	gamma, vacuum	Spinks and Woods 1976
"	liquid	3.5	0.1	0.4	4.5	alpha, vacuum	IEEE S-146 1963
"	liquid	4.1	0.1	0.4	4.6	alpha, vacuum	Hall 1963
1-propanol	liquid	4.4			4.4	gamma, vacuum	Spinks and Woods 1976
"	liquid	2.8	0.1	0.1	3.0	alpha, vacuum	Hall 1963
2-propanol	liquid	3.7		1.5	5.2	gamma, vacuum	Spinks and Woods 1976
n-propanol	liquid	2.8		0.1	3.9	alpha, vacuum	IEEE S-146 1963
1-butanol	liquid	4.6			4.6	gamma, vacuum	Spinks and Woods 1976
"	liquid	3.6	0.1	0.1	4.3	alpha, vacuum	Hall 1963
t-butanol	liquid	1.0		3.6	4.6	gamma, vacuum	Spinks and Woods 1976
n-butanol	liquid	3.6		0.1	4.3	alpha, vacuum	IEEE S-146 1963
1-octanol	liquid	3.5	0.1	< 0.1	3.7	alpha, vacuum	Hall 1963
1-decanol	liquid	3.5	< 0.1	< 0.1	3.6	alpha, vacuum	Hall 1963

Table D.5b Radiolytic G Values for Various Oxygenated Compounds at 298 K

Compound	Phase	G(H ₂)	G(CO)	G(CH ₄)	G(gas)	Experimental Conditions	References
<i>Ethers:</i>							
ethyl ether	liquid	3.4	NA	0.4	3.8	gamma, vacuum	Spinks and Woods 1976
"	liquid	3.6	0.1	0.2	3.9	alpha, vacuum	Hall 1963
ethyl n-butyl ether	liquid	3.3	0.1	0.1	3.5	alpha, vacuum	Hall 1963
dibutyl ether	liquid	2.9	NA	0.1	3.0	gamma, vacuum	Spinks and Woods 1976
n-butyl ether	liquid	2.7	0.1	0.1	2.9	alpha, vacuum	Hall 1963
ethyl tertbutyl ether	liquid	2.0	0.1	0.8	2.9	alpha, vacuum	Hall 1963
isopropyl ether	liquid	2.2	< 0.1	1.5	8.4	gamma, vacuum	Newton 1963
"	liquid	2.4	0.1	0.9	5.8	alpha, vacuum	Newton 1963
d-isopropyl ether	liquid	2.4	NA	1.7	4.1	gamma, vacuum	Spinks and Woods 1976
dioxan	liquid	2.1	0.3	NA	2.4	gamma, vacuum	Spinks and Woods 1976
tetrahydrofuran	liquid	2.6	NA	NA	2.6	Gamma, vacuum	Spinks and Woods 1976
<i>Aldehydes & Ketones:</i>							
propion-aldehyde	liquid	1.2	1.6	0.1	4.4	electron, vacuum	Hall 1963
acetone	liquid	0.96	0.56	1.76	3.62	60-Co-gamma	Spinks and Woods 1976
"	liquid	1.47	0.8	0.97	3.86	6.9 MeV He ions	Spinks and Woods 1976
"	liquid	2.36	1.05	0.99	5.17	67 MeV C-ions	Spinks and Woods 1976
"	liquid	2.71	1.22	0.96	5.77	65.7 MeV N ions	Spinks and Woods 1976
"	liquid	1.0	0.6	1.8	3.6	gamma, vacuum	Spinks and Woods 1976
"	liquid	1.5	0.8	1.0	3.9	alpha, vacuum	Spinks and Woods 1976
"	liquid	0.9	0.8	2.6	4.8	gamma, vacuum	Hall 1963
methyl ethyl ketone	liquid	1.2	0.8	0.9	6.8	gamma, vacuum	Hall 1963
diethyl ketone	liquid	1.2	1.5	0.1	7.7	gamma, vacuum	Hall 1963

Table D.5c Radiolytic G Values for Various Oxygenated Compounds at 298 K

Compound	Phase	G(H ₂)	G(CO)	G(CH ₄)	G(gas)	Experimental Conditions	References
<i>Carboxylic Acids:</i>							
acetic acid	liquid	0.5	0.2	3.9	10.5	gamma, vacuum	Spinks and Woods 1976
"	liquid	0.5	0.4	1.4	7.2	alpha, vacuum	Spinks and Woods 1976
propionic acid	liquid	0.8	0.3	0.5	5.5	alpha, vacuum	Hall 1963
<i>Esters:</i>							
methyl acetate	liquid	0.8	1.6	2.0	5.7	gamma, vacuum	Spinks and Woods 1976
"	liquid	0.9	1.6	2.1	5.6	gamma, vacuum	Hall 1963
"	liquid	0.6	1.2	0.8	3.4	electron, vacuum	Hall 1963
ethyl acetate	liquid	0.9	1.1	1.6	3.6	gamma, vacuum	Hall 1963
isopropyl acetate	liquid	0.9	1.2	0.9	5.6	alpha, vacuum	Hall 1963
"	liquid	0.5	0.8	1.0	3.6	electron, vacuum	Hall 1963
n-propyl acetate	liquid	0.8	1.1	0.4	4.0	electron, vacuum	Hall 1963
benzyl acetate	liquid	0.1	0.2	0.8	2.7	electron, vacuum	Hall 1963
di(2-ethyl) hexyl sebacate	liquid	1.0	0.3	< 0.1	1.8	electron, vacuum	IEEE S-146 1963
"	liquid	1.0	0.3	< 0.1	1.5	gamma, vacuum	Arakawa et al. 1983
di(2-ethyl- hexyl) adipate	liquid	0.9	0.5	< 0.1	1.7	gamma, vacuum	Arakawa et al. 1983
pentaerythritol ester	liquid	0.8	0.8	< 0.1	1.9	gamma, vacuum	Arakawa et al. 1983
<i>Phosphate Esters:</i>							
tricresyl phosphate	liquid	0.05	< 0.1	< 0.1	0.06	gamma, vacuum	Arakawa et al. 1983
tributyl phosphate	liquid	2.0	NA	0.3	2.3	gamma	Holland et al. 1978

Table D.6 Radiolytic G Values for Halogenated Hydrocarbons at 298 K

Compound	Phase	G(H ₂)	G(HCl)	G(F ₂)	G(gas)	Experimental Conditions	References
carbon tetrachloride	liquid	0.7-0.8	0.7-0.8	NA	NA	gamma, vacuum	Spinks and Woods 1976; IEEE S-146 1963
"	liquid	NA	NA	NA	8.6	gamma, oxygen	Spinks and Woods 1976
"	liquid	NA	NA	NA	0.6	alpha, air	Kazanjan 1976
chlorobenzene	liquid	< 0.1	1.4	< 0.1	1.4	gamma, vacuum	Spinks and Woods 1976
bromobenzene	liquid	< 0.1	2.3	0.2	2.5	gamma, vacuum	Spinks and Woods 1976
iodobenzene	liquid	< 0.1	< 0.1	2.0	2.0	gamma, vacuum	Spinks and Woods 1976
111-trichloroethane	liquid	0.2	NA	NA	0.7	alpha	Kazanjan 1976
"	liquid	NA	0.4	NA	NA	gamma	Getoff and Lutz 1985
Freons	liquid	NA	NA	NA	2.6 max	gamma	Alfassi 1982; Alfassi and Heusinger 1983
chloroform	liquid	NA	5-11	NA	NA	gamma, vacuum	Ottolenghi and Stein 1961; Chen et al. 1960
methylene chloride	liquid	NA	4.9	NA	NA	gamma, vacuum	IEEE S-146 1963
trichloroethylene	liquid	NA	0.25	NA	NA	gamma, vacuum	Kazanjan and Horrell 1971; Kazanjan and Brown 1969
"	liquid	NA	G(H ⁺)= 4600	NA	NA	gamma, O ₂	Kazanjan and Brown 1969

Table D.7 Radiolytic G values for Organic Nitrogen Compounds at 298 K

Compound	Phase	G(H ₂)	G(gas)	Experimental Conditions	References
nitromethane	liquid	NA	2.0	gamma, vacuum	Spinks and Woods 1976
nitrobenzene	liquid	NA	0.16	gamma, vacuum	Spinks and Woods 1976
acetonitrile	liquid	0.67	1.52	gamma, vacuum	Spinks and Woods 1976
methylamine	liquid	5.4	5.58	gamma, vacuum	Spinks and Woods 1976
aniline	liquid	0.12	0.41	gamma, vacuum	Spinks and Woods 1976
propionamide	liquid	0.14	3.67	gamma, vacuum	Spinks and Woods 1976
pyrrole	liquid	0.2	NA	gamma, vacuum	Spinks and Woods 1976
3-pyrroline	liquid	2.34	NA	gamma, vacuum	Spinks and Woods 1976
pyrrolidine	liquid	6.35	NA	gamma, vacuum	Spinks and Woods 1976
pyrazole	liquid	0.04	0.16	gamma, vacuum	Spinks and Woods 1976
tetrazole	liquid	trace	0.96	gamma, vacuum	Spinks and Woods 1976
pyridine	liquid	0.025	NA	gamma, vacuum	Spinks and Woods 1976
pyrimidine	liquid	0.03	NA	gamma, vacuum	Spinks and Woods 1976
mono-n-butylamine	liquid	5.6	10.1	gamma, G(HC)=0.5* G(NH ₃)=4.0	Mirichi 1981
dibutylamine	liquid	3.6	NA	gamma, G(HC)=0.5	Mirichi 1981
tri-n-butyl amine	liquid	2.7	NA	gamma, G(HC)=0.5,	Mirichi 1981

note: HC indicates hydrocarbon gases

Table D.8 Radiolytic G Values for Common Commercial Lubricants at 298 K

Lubricant	Radiation	G Values	Experimental Conditions	References
Silicones	gamma	$G(\text{gas})=2.3$; $G(\text{H}_2)=0.6$; $G(\text{CH}_4)=1.4$; $G(\text{C}_2\text{H}_6)=0.3$	vacuum	Arakawa et al. 1983
Texaco Regal-A motor oil	alpha	$G(\text{gas})=2.9$; $G(\text{H}_2)=2.8$; $G(\text{HC})=0.1$	air, mixed w/ calcium silicate to form paste	Kazanjan 1976
"	gamma	$G(\text{H}_2)=2.3$	vacuum; 8.4 Mrad	Kazanjan and Brown 1969
"	gamma	$G(\text{H}_2)=1.8$	500 torr O_2 ; 8.4 Mrad	Kazanjan and Brown 1969
"	gamma	$G(\text{H}_2)=2.1$	500 torr O_2 ; 1.4 Mrad	Kazanjan and Brown 1969
DuoSeal vacuum pump oil	alpha (Pu-238)	$G(\text{gas})=1.7$; $G(\text{H}_2)=1.6$	air, sorbed on vermiculite	Zerwekh 1979
"	alpha (Cm-244)	$G(\text{gas})=2.8$; $G(\text{H}_2)=2.7$; $G(\text{CO}_2)=0.1$	air	Bibler and Orebaugh 1978
"	gamma	$G(\text{gas})=2.1$; $G(\text{H}_2)=2.0$; $G(\text{CO}_2)=0.1$	air	Bibler and Orebaugh 1978
Rycon lubricating grease	gamma (Co-60)	$G(\text{H}_2)=1.0$	vacuum & air	Kazanjan and Brown 1969

Table D.9 Radiation Resistance of Some Common Polymers at 298 K

(listed in order of decreasing resistance to net molecular-weight change)

Radiation resistance of common polymers that predominately crosslink	
Polymer	Characteristics
poly(vinyl carbazole)	aromatic, N in main chain
polystyrene	aromatic
aniline-formaldehyde	aromatic, N in main chain
nylon	N in main chain (amide)
polymethyl acrylate	ester
polyacrylonitrile	C-N triple bond
styrene-butadiene rubber	aromatic, unsaturated
polybutadiene	unsaturated
polyisoprene	unsaturated
nitrile-butadiene rubber	C-N triple bond, unsaturated
polyethylene oxide	ether
polyvinyl acetate	ester
polyvinyl methyl ether	ether
polyethylene	saturated
silicone	saturated
Radiation resistance of common polymers that are borderline between predominant crosslinking and scission	
Polymer	Characteristics
polysulfide rubber	S in main chain
polyethylene terephthalate	aromatic, ester
polyvinyl chloride	halogen
polyvinylidene chloride	halogen
polypropylene	saturated
Radiation resistance of common polymers that predominately scission	
Polymer	Characteristics
phenol-formaldehyde	aromatic
polymethyl methacrylate	ester
polyvinyl alcohol	alcohol
polytetrafluoroethylene	halogen
polyisobutylene	saturated
cellulose	alcohol/ether

Table D.10 Expected Relative G(flam gas) Values for Structurally Related Polymers Containing Only Carbon, Hydrogen, Nitrogen, and Oxygen

High [liquid G(flam gas) = 5 - 7]
hydrocarbon polymers containing only saturated C-C bonds
Polymers containing alcohol functional groups
Polymers containing ether functional groups
Medium [liquid G(flam gas) = 2 - 3]
Hydrocarbon polymers containing unsaturated C-C bonds
Polymers containing ester functional groups
Low [liquid G(flam gas) < 1]
Polymers with aromatic characteristics

Table D.11 Summary of Maximum G Values for Various Classes of Polymers at 298 K^a

Group	Polymer	G(H ₂)	G(flam gas)	G(net gas) ^b
Saturated-Hydrocarbons	polyethylene	4.0	4.1	4.1
	polypropylene	3.3	3.4	3.4
	ethylene-propylene	c	c	c
Alcohols	polyisobutylene	1.6	2.4	2.4
	polyvinyl alcohol	3.1	3.1	3.1
	polyethylene glycol	3.5	3.5	3.5
Ethers	cellulose	3.2	3.2	10.2
	cellulose nitrate	d	d	6.0 ^e
	urea formaldehyde	2.4	2.8	2.8
	polyoxymethylene	2.1	5.6	14.1
	polypropylene oxide	1.1	d	d
	polyvinyl formal	d	d	5.6 ^e
	polybutadiene	0.5	0.5	0.5
Unsaturated - Hydrocarbons	polyisoprene	0.7	0.9	0.9
Esters	polymethyl methacrylate	0.4	2.0	4.1
	polyvinyl acetate	0.9	1.4	1.4
Aromatics	polystyrene	0.2	0.2	0.2
	polysulfone	0.1	0.1	0.1
	polycarbonate	< 0.1	< 0.1	0.9
	polyesters	0.3	0.3	< 0.8
	polyphenyl methacrylate	< 0.1	< 0.1	1.3
Halogen - Containing Polymers	polyvinyl chloride	0.7	0.7	2.6
	polychloroprene	0.1	0.1	0.7
	chlorosulfonated polyethylene	0.3	0.3	0.6
	polychlorotrifluoroethylene	0	0	1.1
	polytetrafluoroethylene	0	0	< 0.3
	chlorinated polyether	0.7	0.8	0.8
	rubber hydrochloride	0	0	< 2.1
	polyvinylidene chloride	0	0	< 2.1
Miscellaneous	polyamides	1.1	1.2	1.5
	ion exchange resins	1.7	1.7	2.1

a Values listed are those most appropriate for TRU waste, i.e., above 10 Mrad absorbed dose or for commercial rather than for pure materials.

b G(net gas) is the net G value, and includes depletion of oxygen when applicable.

c Values are intermediate between those for polyethylene and those for polypropylene.

d Not reported.

e Calculated on the basis of $G(\text{gas}) = [\text{factor}] \times G(\text{gas})_s$ for polyethylene, factor=1.5 for cellulose nitrate and factor=1.4 for polyvinyl formal, and $G(\text{gas})=4.1$ for polyethylene.

Table D.12 G(gas) Values for Miscellaneous Commercial Plastics

Material	G(gas)	Material	G(gas)
cellulose nitrate	6.2	melamine formaldehyde w/ cellulosic filler	0.8
polyvinyl formal	5.7	Selectron 5038 polyester	0.8
polyethylene	4.1	natural rubber w/ fillers	< 0.8
allyl diglycol carbonate	2.6	natural rubber	0.4
ethyl cellulose	2.1	Thiokol ST	0.4
methyl methacrylate	2.1	Neoprene	< 0.25
cellulose propionate	2.1	casein plastic	0.2
cellulose acetate butyrate	1.6	Mylar ® film	0.2
nylon	1.6	Plaskon alkyd	0.12
phenolics (no fillers)	< 1.2	triallyl cyanurate	0.12
urea formaldehyde w/ cellulostic filler	1.2	aniline formaldehyde	0.04
Silastic	1.2	furane resin (asbestos & carbon filler)	< 0.04
cellulose acetate	1.2	polystyrene	< 0.04
butyl rubber	1.2	styrene-butadiene copolymer	< 0.04
natural rubber	< 1.2		

Table D.13 Summary of Radiolysis Experiments on Cements at 298 K

Cement Type	Source	Radiolysis Products / Comments	References
high-alumina cement	gamma (Co-60)	Steady-state H_2 pressure was dose dependent, O_2 partially consumed, equilibrium pressure in descending order for: Fe_2O_3 cement > neat cement > MnO_2 cement	Bibler 1976; Bibler 1978
high-alumina cement	alpha	H_2 and O_2 produced, O_2 was 20-50% of total gas, no steady-state pressure up to 200 psi, $G(H_2)_{avg}=0.21$	Bibler 1978
high-alumina cement w/ NO_3^- or NO_2^-	gamma	No additional pressurization as compared to high-alumina cement without the nitrates. At low dose rates (0.09 Mrad/hr) O_2 was consumed, and at high dose rates (28 Mrad/hr) O_2 was generated. No steady state pressure was reached.	Bibler 1978
Portland cement/gypsum-perlite plaster in ratio 1.7:1.0 with water	gamma	$G(H_2)=0.03$, hydrogen was the only gas produced, steady-state pressure was dose rate dependent, O_2 in air was partially consumed, and nitrogen was unaffected	Bibler and Orebaugh 1978
Portland cement / gypsum-perlite plaster in ratio 1.7:1.0 with water	alpha: (Cm-244)	$G(H_2)=0.6$, hydrogen generation was not dose rate dependent, oxygen was partially consumed, nitrogen was unaffected, no steady state pressure was obtained up to 200 psi.	Bibler and Orebaugh 1978
concrete	incinerator ash	With 35% water (by mass) $G(H_2)=0.38$, after drying at 200°C to obtain 7.4% water $G(H_2)=0.0002$. Conclusion was that water of hydration is not nearly as easily degraded as free water.	Bibler and Orebaugh 1978
cement-based grouts	alpha: simulated current acid waste	The simulated waste was acidic and contained metal sulfates and nitrates. The cement was low-alumina cement. $G(gas)=0.32-0.43$. (After samples were dried at an elevated temperature, no radiolysis gases were evolved.) A portion of the gas evolved was hydrogen.	Dole and Friedman 1986
cement-based grouts	alpha: simulated double-shell slurry waste	The simulated waste was acidic and contained metal sulfates and nitrates. The cement was low-alumina cement. $G(gas)=0.04-0.15$. A portion of the gas evolved was hydrogen.	Dole and Friedman 1986
cement-based grouts	gamma: simulated double-shell slurry waste	The simulated waste was acidic and contained metal sulfates and nitrates. The cement was low-alumina cement. $G(gas)=0.02$. A portion of the gas evolved was hydrogen.	Dole and Friedman 1986

APPENDIX E. FLAMMABILITY LIMITS

Table E.1 Lower and Upper Flammability Limits for Common Gases and Vapors

Gas or vapor	Limits in Air (%)	
	Lower	Higher
<i>Inorganic</i>		
Hydrogen	4.1	75
Ammonia	15	28
Hydrazine	4.7	100
Hydrogen sulfide	4.3	45
Hydrogen cyanide	6	41
Cyanogen	6	32
Carbon Disulfide	1.2	50
Carbon Monoxide	23.5	100
<i>Hydrocarbons</i>		
Methane	5.0	14
Ethane	3.0	12.5
Propane	2.2	9.5
Butane	1.9	8.5
Isobutane	1.8	8.4
Pentane	1.4	7.8
Isopentane	1.4	7.6
2-2 Dimethylpropane	1.4	7.5
Hexane	1.2	7.5
Dimethyl butane	1.2	7.0
2-Methyl pentane	1.2	7.0
Heptane	1.1	6.7
2-3 Dimethyl pentane	1.1	6.7
Octane	1.0	-
Iso-octane	1.0	6.0
Methyl cyclohexane	1.2	-
Ehtyl cyclohexane	0.9	6.6
Nonane	0.8	-
Tetramethyl pentane	0.8	4.9
Diethyl pentane	-	5.7
Decane	0.8	5.4
Ethylene	3.1	32
Propylene	2.4	10.3
Butylene	2.0	9.6
Butene-1	1.6	9.3
Butene-2	1.8	9.7
Isobutylene	1.8	8.8

Table E.1. Lower and Upper Flammability Limits for Common Gases and Vapors, continued

Gas or vapor	Limits in Air (%)	
	Lower	Higher
b-n-Amylene	1.5	8.7
Butadiene	2.0	11.5
Acetylene	2.5	81
Benzene	1.4	7.1
Toluene	1.4	6.7
o-Xylene	-	6.0
Ethyl benzene	1.0	-
Styrene	-	6.1
Butyl benzene	-	5.8
Naphthalene	-	5.9
Cyclopropane	2.4	10.4
Ethyl cyclobutane	1.2	7.7
Ethyl cyclopentane	-	6.7
Cyclohexane	-	8
<i>Alcohols</i>		
Methyl alcohol	6.7	36
Ethyl alcohol	3.3	19
n-Propyl alcohol	2.1	13.5
Isopropyl alcohol	2.0	12
n-Butyl alcohol	1.4	11.2
Amyl alcohol	1.2	-
Furfuryl alcohol	1.8	16.3
Allyl alcohol	2.5	18.0
Propylene glycol	2.6	12.5
Triethylene glycol	0.9	9.2
<i>Ethers</i>		
Methyl ether	3.4	18
Ethyl Ether	1.7	48
Ethyl n-propyl ether	1.9	24
Isopropyl ether	1.3	21
Vinyl ether	1.7	28
Ethylene Oxide	3.6	80
Propylene oxide	2.1	21.5
Dioxane	2.0	22

Table E.1. Lower and Upper Flammability Limits for Common Gases and Vapors, continued

Gas or vapor	Limits in Air (%)	
	Lower	Higher
Trioxane	3.6	29
Acetal	1.6	10.4
<i>Acid; Anhydride</i>		
Acetic Acid	5.4	-
Acetic anhydride	2.7	10
Phthalic anhydride	1.7	10
<i>Esters</i>		
Methyl formate	5.0	20
Ethyl formate	2.7	13.5
Butyl formate	1.7	8
Methyl acetate	3.1	16
Ethyl acetate	2.2	9
Vinyl acetate	2.6	13.4
Propyl acetate	1.8	8
Isopropyl acetate	1.8	8
Butyl acetate	1.4	7.6
Amyl acetate	1.1	-
Methyl cellulose acetate	1.7	8.2
Methyl propionate	2.4	13
Ethyl propionate	1.8	11
Methyl lactate	2.2	-
Ethyl lactate	1.5	-
Ethyl nitrate	4.0	-
Ethyl nitrite	3.0	-
<i>Phenols</i>		
Cresol	1.1	-
<i>Amines and Imines</i>		
Methylamine	4.9	20.7
Dimethylamine	2.8	14.4
Trimethylamine	2.0	11.6
Ethylamine	3.5	14.0
Diethylamine	1.8	10.1

Table E.1. Lower and Upper Flammability Limits for Common Gases and Vapors, continued

Gas or vapor	Limits in Air (%)	
	Lower	Higher
Triethylamine	1.2	8.0
Propylamine	2.0	10.4
n-Butyl amine	1.7	9.8
Allylamine	2.2	22
Ethylene imine	3.6	46
Methyl cellulose	2.5	19.8
Ethyl cellulose	1.8	14.0
Butyl cellulose	1.1	10.6
Diethyl peroxide	2.3	-
<i>Aldehydes</i>		
Acetaldehyde	4.1	55
Paraldehyde	1.3	-
Butyraldehyde	2.5	-
Acrolein	2.8	31
Croton aldehyde	2.1	15.5
Furfural	2.1	-
<i>Ketones</i>		
Acetone	2.5	11
Methyl ethyl ketone	1.8	10
Methyl propyl ketone	1.5	8
Methyl butyl ketone	1.3	8
Methyl isobutyl ketone	1.4	7.5
Cyclohexanone	1.1	-
Isophorone	0.8	3.8
<i>Other N Compounds</i>		
Acrylonitrile	3.0	17
Pyridine	1.8	12.4
Nicotine	0.7	4.0
<i>Halogen Derivatives</i>		
Methyl chloride	7.6	17.4
Methyl bromide	13.5	14.5
Methylene chloride	-	-

Table E.1. Lower and Upper Flammability Limits for Common Gases and Vapors, continued

Gas or vapor	Limits in Air (%)	
	Lower	Higher
Ethyl chloride	3.8	15.4
Ethyl bromide	6.7	11.3
Ethylene dichloride	6.2	16
Vinyl chloride	4.0	22
Dichloroethylene	9.7	12.8
Trichloroethylene	-	-
Ethylene chlorohydrin	4.9	15.9
Propyl chloride	2.6	11.1
Propylene dichloride	3.4	14.5
Allyl chloride	3.3	11.1
Allyl bromide	4.4	7.3
2-Chloropropene	4.5	16.0
n-Butyl chloride	1.8	10.1
Butyl bromide	5.2	5.6
Chlorobutene	2.2	9.3
Isocrotyl chloride	4.2	19
Isocrotyl bromide	6.4	12
n-Amyl chloride	1.6	8.6
tert.-Amyl chloride	1.5	7.4
Chlorobenzene	1.3	7.1
Dichlorobenzene	2.2	9.2
<i>Miscellaneous</i>		
Gasoline	1.4	7.6
Naphtha	0.8	5
Coal gas	5.3	32
Kerosine	0.8	5

APPENDIX F. SAMPLE PROBLEMS

Example #1: Calculation of hydrogen gas concentration in a single rigid leaking enclosure

Problem: Consider a rigid container holding radioactive waste that is generating hydrogen gas at a rate of 4.2×10^{-7} gmol/s. Hydrogen gas escapes the container by diffusion through a small opening in the wall of the container. It has been determined experimentally that the effective hydrogen release rate through the opening is 4×10^{-7} gmol H_2 /s-mole fraction. The void volume in the container is 1000 cm^3 , the temperature is 298 K, and the pressure is assumed to be 1 atmosphere. Calculate the hydrogen gas mole fraction as a function of time. How long does it take for the hydrogen mole fraction to reach 0.05 (5 mole percent hydrogen)? How long does it take to reach 19 volume percent hydrogen?

Solution: For this problem, $T = 4 \times 10^{-7}$ gmol/s and $R_M = 4.2 \times 10^{-7}$ gmol/s. Using the ideal gas law the initial number of gas moles is: $n = (1 \text{ atm})(1000 \text{ cm}^3)/(82.05 \text{ atm}\cdot\text{cm}^3/\text{gmol}\cdot\text{K})(298 \text{ K}) = 4.09 \times 10^{-2}$ gmol. Using Equation 4.12 with these values for T , R_M , and n , the mole fraction of hydrogen as a function of time, $X(t)$, is:

$$X(t) = 1.05[1 - \exp(-9.78 \times 10^{-6} t)]$$

This equation can be rearranged to give the time as a function of the hydrogen mole fraction:

$$t = \frac{-\ln\left(1 - \frac{X(t)}{1.05}\right)}{9.78 \times 10^{-6}}$$

From this equation it is determined that the hydrogen mole fraction reaches 0.05 after 4988.8 seconds (~83.1 minutes), and the hydrogen mole fraction reaches 0.19 (19 volume percent) after 2.04×10^4 seconds (~5.67 hours).

Example #2: Single semi-open rigid container w/ contents undergoing radiolysis

Problem: Consider a semi-open rigid container with a void volume of 1000 cm^3 that contains material which radiolytically generates gases. The $G(\text{net gas})$ value is 1.5 molecules/100 eV, the $G(\text{flam gas})$ value is 0.7 molecules/100eV, and the decay heat absorbed by the material radiolytically generating gas is 2 W. Assume that the container initially has no flammable gas, that the temperature is steady at 313 K, and that the pressure outside the container is 1.0 atmosphere. Determine an equation describing the hydrogen mole fraction as a function of time. What is the steady-state hydrogen mole fraction? How long does it take for the hydrogen mole fraction in the container to reach 0.05 (5 volume percent hydrogen)?

Solution: The molar rate of radiolytically generated gas is determined from Equation 4.6:

$$R_M(\text{net gas}) = (2W) \left(\frac{\text{J/s}}{\text{W}} \right) \left(\frac{\text{eV}}{1.602 \times 10^{-19} \text{ J}} \right) \left(\frac{1.5 \text{ molecules/100eV}}{6.023 \times 10^{23} \text{ molecules/gmol}} \right) = 3.11 \times 10^{-7} \text{ gmol/s}$$

The volumetric rate of gas generation is then determined by applying the ideal gas law:

$$Q = \frac{R_M(\text{net gas})}{\rho_M} = \frac{RTR_M(\text{net gas})}{P} = \frac{\left(82.05 \frac{\text{cm}^3 \cdot \text{atm}}{\text{gmol} \cdot \text{K}}\right)(313) \left(3.11 \times 10^{-7} \frac{\text{gmol}}{\text{s}}\right)}{1 \text{ atm}} = 7.99 \times 10^{-3} \frac{\text{cm}^3}{\text{s}}$$

The concentration (or molar density) of flammable gas entering the container is determined from the G-values for net gas and for flammable gas along with the ideal gas law:

$$C_{A0} = \left(\frac{G(\text{flam gas})}{G(\text{net gas})} \right) \left(\frac{P}{RT} \right) = \left(\frac{0.7}{1.5} \right) \left(\frac{1 \text{ atm}}{(82.05 \text{ cm}^3 \cdot \text{atm}/\text{gmol} \cdot \text{K})(313)} \right) = 1.817 \times 10^{-5} \frac{\text{mole flam Gas}}{\text{cm}^3}$$

The equation describing the concentration of flammable gas (moles flammable gas per cubic centimeters) in the container as a function of time is determined using Equation 4.14:

$$C_A = \left(1.817 \times 10^{-5} \text{ gmol/cm}^3 \right) \left[1 - \exp \left(\frac{-(t)(7.99 \times 10^{-3} \text{ cm}^3/\text{s})}{1000 \text{ cm}^3} \right) \right]$$

It is useful to calculate the mole fraction of flammable gas as a function of time. At a pressure of 1 atm and a temperature of 313 K, one cubic centimeter contains $n = [(1 \text{ atm})(1 \text{ cm}^3)/(82.05 \text{ atm} \cdot \text{cm}^3/\text{gmol} \cdot \text{K})(313)] = 3.894 \times 10^{-5}$ gmoles gas. Therefore, the mole fraction of flammable gas as a function of time for this example is:

$$\text{Mole Fraction Flammable Gas} = X(t) = \left(\frac{1.817 \times 10^{-5}}{3.894 \times 10^{-5}} \right) \left[1 - \exp \left(\frac{-t(7.99 \times 10^{-3} \text{ cm}^3/\text{s})}{1000 \text{ cm}^3} \right) \right]$$

For long times the exponential term goes to zero and the steady-state flammable gas mole fraction is 0.467.

The above equation can be rearranged to give the time as a function of the mole fraction flammable gas:

$$t = (-125156.4) \ln(1 - X(t)2.143).$$

From this equation, the flammable gas reaches 5 mole % (mole fraction of 0.05 or 5 volume percent) at a time of about 14.185×10^3 seconds (236.4 minutes).

Example #3: Check of solution to hydrogen gas concentration in a rigid leaking enclosure nested within a rigid non-leaking enclosure

Problem: Prove that the expressions for X_1 and X_2 in Equations 4.19 and 4.20 satisfy the coupled differential equations in 4.2.18a and 4.19b.

Solution: From Equations 4.19 and 4.20, $X_1(t)$ is given by:

$$X_1(t) = \frac{AS}{(A+B)^2} - \frac{AS \exp[-t(A+B)]}{(A+B)^2} + \frac{BS t}{(A+B)}$$

and $X_2(t)$ is given by:

$$X_2(t) = \frac{-BS}{(A+B)^2} + \frac{BS \exp[-t(A+B)]}{(A+B)^2} + \frac{BS t}{(A+B)}.$$

Taking the derivative of X_1 :

$$\frac{d}{dt}[X_1(t)] = \frac{d}{dt} \left[\frac{AS}{(A+B)^2} - \frac{AS \exp[-t(A+B)]}{(A+B)^2} + \frac{BS t}{(A+B)} \right]$$

or

$$\frac{dX_1}{dt} = \frac{AS}{(A+B)^2} (A+B) \exp[-t(A+B)] + \frac{SB}{(A+B)} = \frac{AS \exp[-t(A+B)] + SB}{(A+B)}.$$

Substituting $X_1(t)$, $X_2(t)$, and the above expression for dX_1/dt into Equation 4.18a yields:

$$\begin{aligned} \frac{dX_1}{dt} &= S - A(X_1 - X_2) \\ &= S - A \left\{ \frac{AS(1 - \exp[-t(A+B)])}{(A+B)^2} + \frac{SB t}{A+B} + \frac{BS(1 - \exp[-t(A+B)])}{(A+B)^2} - \frac{SB t}{A+B} \right\} \\ &= S - AS \left\{ \frac{(A+B)(1 - \exp[-t(A+B)])}{(A+B)^2} \right\} = S - \frac{AS}{A+B} + \frac{AS \exp[-t(A+B)]}{A+B} \\ &= \frac{BS}{A+B} + \frac{AS \exp[-t(A+B)]}{A+B} = \frac{AS \exp[-t(A+B)] + SB}{A+B}. \end{aligned}$$

Therefore, with this check and the check that the initial condition on X_1 is satisfied (i.e., $X_1(0)=0$) by the solution, the solution for X_1 is proved valid.

Now, check the solution for X_2 by substituting it into the differential equation for dX_2/dt .

The derivative of X_2 is:

$$\frac{d}{dt}[X_2(t)] = \frac{d}{dt} \left[\frac{-BS}{(A+B)^2} + \frac{BS \exp[-t(A+B)]}{(A+B)^2} + \frac{BS t}{(A+B)} \right]$$

or

$$\frac{dX_2}{dt} = \frac{-BS(A+B) \exp[-t(A+B)]}{(A+B)^2} + \frac{SB}{A+B} = \frac{SB [1 - \exp[-t(A+B)]]}{A+B}$$

Substituting X_1 , X_2 , and the above expression for dX_2/dt into Equation 4.18b:

$$\begin{aligned}
 \frac{dX_2}{dt} &= B(X_1 - X_2) \\
 &= B \left\{ \frac{AS(1 - \exp[-t(A+B)])}{(A+B)^2} + \frac{SBt}{A+B} + \frac{BS(1 - \exp[-t(A+B)])}{(A+B)^2} - \frac{SBt}{A+B} \right\} \\
 &= BS \left\{ \frac{(A+B)(1 - \exp[-t(A+B)])}{(A+B)^2} \right\} = \frac{BS[1 - \exp[-t(A+B)]]}{A+B}
 \end{aligned}$$

Therefore, with this check and the check that the initial condition on X_2 is satisfied (i.e., $X_2(0)=0$) by the solution, the solution for X_2 is proved valid.

Example #4: Hydrogen gas concentration in a rigid leaking enclosure nested within a rigid non-leaking enclosure

Problem: Consider a leaking container with contents that have a decay heat of 2.26 W (1.41×10^{19} eV/s) and an effective radiolytic G-value for hydrogen generation of 0.7 molecules $H_2/100\text{eV}$. The leak in the container has been determined to allow a flux of $T_1 = 1.1 \times 10^{-7}$ gmol $H_2/\text{s}\cdot\text{mole fraction}$. The leaking container is nested within a nonleaking container. The void volume of the inner container is 1.0 liter, and the void volume in the outer container (excluding the inner container) is 2.0 liters. Assume that the temperature of the system is constant at 330 K and that the only radiolysis gas produced is hydrogen. How long does it take for the inner container to reach 5 volume percent hydrogen if it is assumed that there is initially no hydrogen in either container.

Solution: Given a decay heat of 1.41×10^{19} eV/s and a G-value of 0.7 molecules $H_2/100$ eV, the hydrogen generation rate is 9.87×10^{16} molecules H_2/s or $R_M = 1.64 \times 10^{-7}$ gmol H_2/s , which is calculated using Equation 4.6. If it is assumed that the containers were filled at 1 atmosphere and 298 K, then the initial number of gas moles are: $n_1 = 4.09 \times 10^{-2}$ gmol and $n_2 = 8.18 \times 10^{-2}$ gmol, where n_1 is the original number of gas moles within the inner enclosure and n_2 is the initial number of gas moles in the void volume within the outer enclosure. Therefore, $S = R_M/n_1 = 4.01 \times 10^{-6}$, $A = T_1/n_1 = 2.69 \times 10^{-6}$, and $B = T_1/n_2 = 1.34 \times 10^{-6}$. Using these numerical inputs and the equation for $X_1(t)$ given by Equation 4.19, the time to reach $X_1 = 0.05$ is determined implicitly to be approximately 211.3 minutes or about 3.5 hours. For this problem, the time to reach a given hydrogen mole fraction can be determined in various ways, including: (1) graphical techniques; (2) trial-and-error methods; or (3) iterative methods (Newton scheme).

Example #5: Hydrogen concentration in two nested rigid leaking containers

Problem: Consider a leaking container with contents that have a decay heat of 2.26 W (1.41×10^{19} eV/s) and an effective radiolytic G-value for hydrogen generation of 0.0131 molecules $H_2/100\text{eV}$ that is nested within a second leaking container. The leak in the inner container has been determined to allow a flux of $T_1 = 1.1 \times 10^{-7}$ gmol $H_2/\text{s}\cdot\text{mole fraction}$, and the outer container has been determined to allow a hydrogen flux of $T_2 = 1.2 \times 10^{-7}$ gmol $H_2/\text{s}\cdot\text{mole fraction}$. The void volume of the inner container is 1.5 liters, and the void volume in the outer container (excluding the inner container) is 2.5 liters. Assume that the temperature of the system is constant at 330 K and that the only radiolysis gas produced is hydrogen. How long does it take for the inner container to reach 4 volume percent hydrogen if it is assumed that there is initially no hydrogen in either container? What is the hydrogen percent by volume in the outer container (excluding the inner container) when the inner container has 5 volume percent hydrogen?

Solution: The coupled differential equations describing the hydrogen concentration in two nested rigid leaking enclosures are given by Equations 4.23a and 4.23b. The solutions for Equations 4.23a and 4.23b are given by Equation 4.24 and 4.250. With a decay heat of 1.41×10^{19} eV/s and a G-value for hydrogen generation of 0.0131 molecules H_2 /100 eV, the hydrogen generation rate is $R_M = 3.0675 \times 10^{-9}$ gmol H_2 /s. If it is assumed that the containers were filled at 1 atmosphere and 298 K, then the initial number of gas moles within the two enclosures are: $n_1 = 6.135 \times 10^{-2}$ gmol and $n_2 = 0.1022$ gmol. Therefore, $S = R_M/n_1 = 5.0 \times 10^{-8}$, $A = T_1/n_1 = 1.79 \times 10^{-6}$, $B = T_1/n_2 = 1.076 \times 10^{-6}$, and $C = T_2/n_2 = 1.174 \times 10^{-6}$. With these numerical inputs, $Z = 4.043 \times 10^{-6}$, and $W = 2.815 \times 10^{-6}$. Then, using these inputs to Equation 4.24 for $X_1(t)$ and Equation 4.25 for $X_2(t)$, the hydrogen concentration for the two containers as a function of time can be determined. See Figure F.1 for the graphical results.

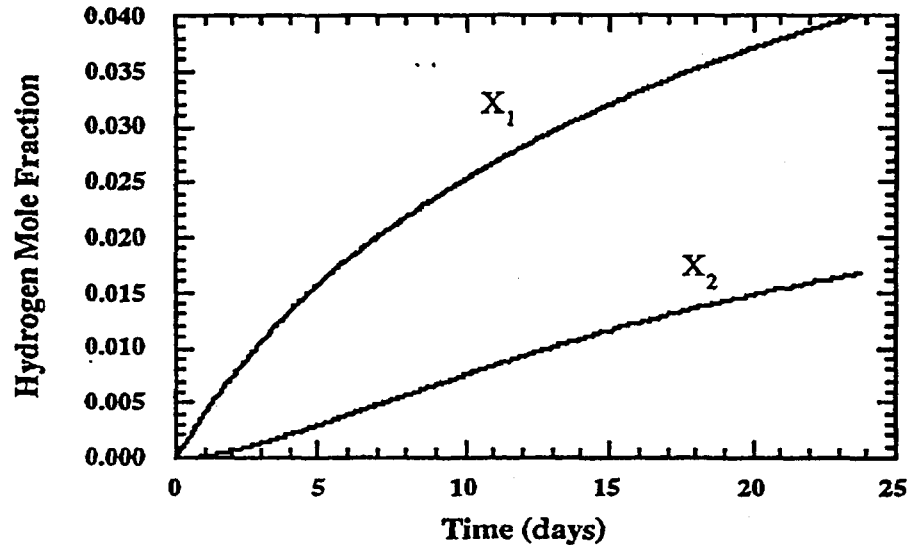


Figure F.1 Hydrogen concentration as a function of time

From the numerical results used to generate the above plot, it is determined that the inner container reaches 4 volume percent hydrogen (mole fraction hydrogen of 0.04) after about 23.8 days, and that at this time the outer container has about 1.7 volume percent hydrogen.

Example #6: Pressure in a single rigid non-leaking container with contents undergoing radiolysis

Problem: Consider a case where the container was sealed at a pressure $P_0 = 1$ atm and a temperature $T_0 = 25^\circ\text{C}$ (298 K). The decay heat absorbed by the material undergoing radiolysis is $D_H = 6.24 \times 10^{20}$ eV/s, the container temperature is 90°C (363 K), the effective net gas radiolytic G values is $G(\text{net gas}) = 0.3$ molecules/100eV, and the container void volume is 5 liters (5000 cm^3). Calculate the container pressure as a function of time. How long does it take for the container to reach a pressure of 2 atmospheres?

Solution: The pressure as a function of time (from Equation 4.47) is:

$$P(t) = \left[1 \text{ atm} \left(\frac{363 \text{ K}}{298 \text{ K}} \right) \right] + \left(\frac{6.24 \times 10^{20} \frac{\text{eV}}{\text{s}}}{100} \right) \left(\frac{0.3 \frac{\text{molecules}}{100 \text{ eV}}}{6.023 \times 10^{23} \frac{\text{molecules}}{\text{gmol}}} \right) \left(\frac{(82.05 \frac{\text{cm}^3 \cdot \text{atm}}{\text{gmol} \cdot \text{K}})(363 \text{ K})}{5000 \text{ cm}^3} \right) (t)$$

or after simplification:

$$P(t) = 1.22 \text{ atm} + \left(1.85 \times 10^{-5} \frac{\text{atm}}{\text{s}} \right) (t).$$

From this equation, the pressure will reach 2 atm in 4.226×10^4 seconds or about 11.7 hours.

Example #7: Pressure in a Single Rigid Leaking Container with Contents Undergoing Radiolysis

Problem: Consider an example of a single leaking enclosure that has a single leakage hole with a length of 0.5 cm and a diameter of 3.2×10^{-3} cm. The container was initially sealed at 25°C, but has a steady state temperature of 80°C. Assume that (1) the effective radiolytic G value is 0.8 molecules/100 eV; (2) the contents decay heat is 2.5 W and all decay heat is absorbed by the material capable of undergoing radiolysis; (3) the void volume of the container is 1000 cm³; (4) the effective viscosity of the gas is 0.021 cP, and (5) the effective molecular weight of the gas within the container at any time can be approximated by 26 g/gmol. Assuming the downstream pressure is one atmosphere, calculate the container pressure as a function of time and the maximum container pressure.

Solution: First it is useful to determine if the contribution to the flow from molecular flow can be neglected. Forming the ratio F_c/F_m :

$$\frac{F_c}{F_m} = \frac{654 D P_u}{m \sqrt{T/M_w}} = \frac{(654)(3.2 \times 10^{-3})(P_u + 1)}{(2)(0.021) \sqrt{353/26}} = 13.5(P_u + 1),$$

it is clear that for $P_u \geq 1$ atm, then $F_m \leq (F_c/27)$ or F_m is about 3.7% of F_c . Therefore, the contribution to the total flow rate from molecular flow can reasonably be neglected. By neglecting molecular flow, the calculated container pressure is conservative and bounding.

Neglecting molecular flow, the equation for the container pressure as a function of time (from Eqn. 4.61) is:

$$P_u(t) = \sqrt{\left(\frac{2R_g T R_M}{F_c} + P_d^2 \right)} \left\{ \tanh^{-1} \left[\frac{t \left(\frac{F_c}{2V} \right) \sqrt{\left(\frac{2R_g T R_M}{F_c} + P_d^2 \right)}}{\sqrt{\left(\frac{2R_g T R_M}{F_c} + P_d^2 \right)}} \right] + \tanh^{-1} \left[\frac{TP_0}{T_0 \sqrt{\left(\frac{2R_g T R_M}{F_c} + P_d^2 \right)}} \right] \right\}.$$

Substituting $F_c = 2.487 \times 10^{-2}$, $V = 1000 \text{ cm}^3$, $R = 82.05 \text{ cm}^3 \cdot \text{atm} / \text{gmol} \cdot \text{K}$, $R_M = 2.073 \times 10^{-7} \text{ gmol/s}$, $T_0 = 298 \text{ K}$, $T = 353 \text{ K}$, $P_d = 1 \text{ atm}$, $P_0 = 1 \text{ atm}$ into the above equation and plotting the results gives the curve in Figure F.2.

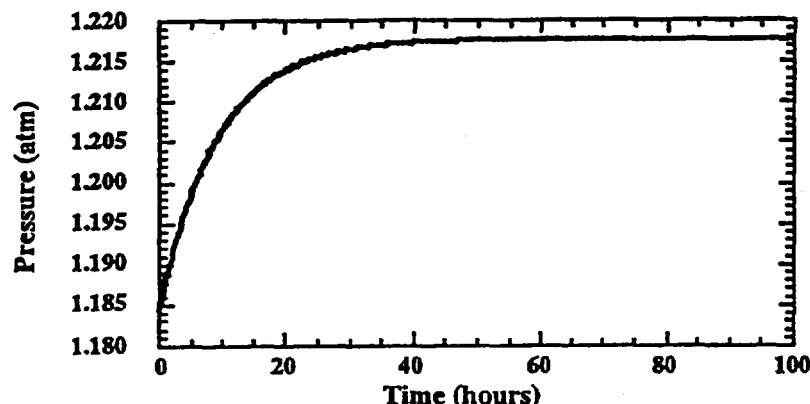


Figure F.2 Pressure as a function of time for example single leaking container

The results shown in Figure F.2 indicate that the container reaches its maximum pressure after about 50 hours and that the maximum pressure is a little less than 1.218 atm. An exact calculation of the steady state pressure shows that $P_{ss}=1.2177$.

Example #8: Lower flammability limit for natural gas in air

Problem: What is the lower flammability limit of natural gas in air?

Solution: Natural gas has an approximate composition of 80% methane (lower limit, 5.3%), 15% ethane (lower limit 3.22%), 4% propane (lower limit 2.37%), and 1% butane (lower limit 1.86%). Using Equation 4.65, the lower limit of the natural gas mixture is:

$$F_{L,MIX} = \frac{100}{\frac{80}{5.3} + \frac{15}{3.22} + \frac{4}{2.37} + \frac{1}{1.86}} = 4.55\%.$$

Example #9: Time to reach 5 volume percent hydrogen in a package with radioactive material nested within three confinement layers and a non-leaking rigid containment vessel

Problem: Consider a mass of radioactive material that has a decay heat of 1×10^{18} eV/s and a G-value for radiolysis of 0.5 molecules/100 eV. The material is first placed in a metal "product can" that allows a hydrogen flux of $T_1=8.0 \times 10^{-7}$ gmol H_2 /s/mole fraction and, is then placed in two plastic bags that each allow a hydrogen flux of 5.0×10^{-7} gmol H_2 /s/mole fraction. This "bagged-out" material is then placed in a rigid non-leaking containment vessel. If the material is sealed in the containment vessel at 298 K, the void volume within the product can is 0.5 liters, the void volume between the outer bag and the containment vessel is 1.5 liters, and the temperature is constant at 330 K, how long does it take for the hydrogen mole fraction within the product can to reach 0.05 (5 volume percent hydrogen)? Assume that the only gas produced is hydrogen.

Solution: For a decay heat of 1×10^{18} eV/s and a G-value of 0.5 molecules H_2 /100 eV, the hydrogen generation rate is $R_M=8.3 \times 10^{-9}$ moles H_2 /s. For the three confinement layers (metal can and two plastic bags), the effective hydrogen flux is $1/T_{eff}=(1/8.0 \times 10^{-7})+(1/5 \times 10^{-7})+(1/5 \times 10^{-7})$, or $T_{eff}=1.9 \times 10^{-7}$ gmol H_2 /s/mole fraction. Using this effective allowable flux through the three confinement layers, the problem

can be visualized as a radioactive mass within one confinement layer (representing the three confinement layers) that is within a non-leaking rigid containment vessel. The solution to this case is given by Equation 4.19, which gives the hydrogen mole fraction as a function of time for the inner-most confinement layer. The number of gas moles originally within the confinement volumes is calculated with the ideal gas equation as $n_1=2.05 \times 10^{-2}$ gmol, and the number of gas moles between the confinement layers and the containment vessel is $n_2=1.16 \times 10^{-2}$ gmol. Using these values, $S=(R_M/n_1)=8.1 \times 10^{-6}$, $A=(T_{eff}/n_1)=9.3 \times 10^{-6}$, and $B=(T_{eff}/n_2)=3.1 \times 10^{-6}$. Then, the hydrogen mole fraction as a function of time is as shown in Figure F.3.

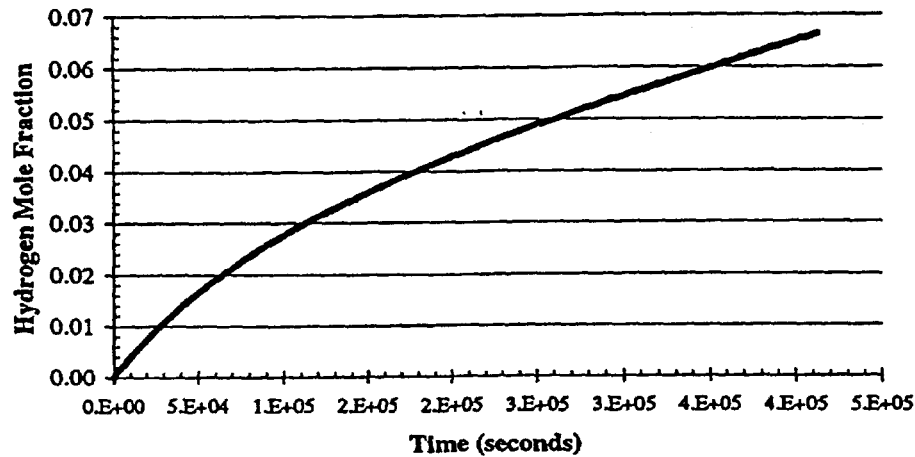


Figure F.3 Hydrogen mole fraction as a function of time

From the plot, the hydrogen mole fraction in the innermost confinement layer reaches 0.05 in about 2.6×10^5 seconds or about 72.2 hours.

BIBLIOGRAPHIC DATA SHEET

(See instructions on the reverse)

1. REPORT NUMBER
(Assigned by NRC, Add Vol., Supp., Rev.,
and Addendum Numbers, if any.)

NUREG/CR-6673

2. TITLE AND SUBTITLE

Hydrogen Generation in TRU Waste Transportation Packages

3. DATE REPORT PUBLISHED

MONTH | YEAR

May | 2000

4. FIN OR GRANT NUMBER

A0291

5. AUTHOR(S)

B.L. Anderson
M.K. Sheaffer
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6. TYPE OF REPORT

Technical

7. PERIOD COVERED (Inclusive Dates)

8. PERFORMING ORGANIZATION - NAME AND ADDRESS (If NRC, provide Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address; if contractor, provide name and mailing address.)

Lawrence Livermore National Laboratory
7000 East Avenue
Livermore, CA 94550

9. SPONSORING ORGANIZATION - NAME AND ADDRESS (If NRC, type "Same as above"; if contractor, provide NRC Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address.)

Spent Fuel Project Office
Office of Nuclear Material Safety and Safeguards
U.S. Nuclear Regulatory Commission
Washington, DC 20555-0001

10. SUPPLEMENTARY NOTES

11. ABSTRACT (200 words or less)

This document addresses hydrogen generation in TRU waste transportation packages. The potential sources of hydrogen generation are summarized with a special emphasis on radiolysis. After defining various TRU wastes according to groupings of material types, bounding radiolytic G-values are established for each waste type. Analytical methodologies are developed for prediction of hydrogen gas concentrations for various packaging configurations in which hydrogen generation is due to radiolysis. Representative examples are presented to illustrate how analytical procedures can be used to estimate the hydrogen concentration as a function of time. Methodologies and examples are also provided to show how the time to reach a flammable hydrogen concentration in the innermost confinement layer can be estimated. Finally, general guidelines for limiting the hydrogen generation in the payload and hydrogen accumulation in the innermost confinement layer are described.

12. KEY WORDS/DESCRIPTORS (List words or phrases that will assist researchers in locating the report.)

transportation, transuranic, radioactive waste, flammable gas, hydrogen generation

13. AVAILABILITY STATEMENT

unlimited

14. SECURITY CLASSIFICATION

(This Page)

unclassified

(This Report)

unclassified

15. NUMBER OF PAGES

16. PRICE

UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D.C. 20555-0001



SPECIAL STANDARD MAIL
POSTAGE AND FEES PAID
USNRC
PERMIT NO. G-67

Key Words:

Grout

Russian Experience

High-Level Waste Tank Closure

Retention: Permanent

RUSSIAN GROUTING EXPERIENCE (U)

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REPORT DATE: MAY 13, 2002

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**Prepared for the U.S. Department of Energy Under
Contract Number DE-AC09-96SR18500**



DISCLAIMER

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Printed in the United States of America

**Prepared For
U.S. Department of Energy**

Key Words:

Grout

Russian Experience

High-Level Waste Tank Closure

RUSSIAN GROUTING EXPERIENCE (U)

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1.0 EXECUTIVE SUMMARY

A final report documenting Russian experience in ambient temperature cement-based waste forms, in-tank waste treatment and grout/concrete decommissioning is provided in Attachment 1. The report is titled "The Review of the Russian Experience on Inorganic Binders for Waste Treatment and Tank Closure," and contains technical information concerning:

- An assessment of the properties of hardened cement materials that affect the performance of hazardous and radioactive waste forms.
- A list of additives used to modify the properties of cement-based waste forms.
- The effect of elevated temperature on hydrated portland cement as a function of time and temperatures up to 180°C.
- The effect of radiation exposure on hydrated cement materials as a function of radiation dose up to 6E+09 Rad. Radiolytic gas generation data is also presented and discussed.
- The results of an experimental investigation on the properties of special grout formulations developed as closure grouts.
- Descriptions of full-scale grouting for decommissioning vessels contaminated with radioactivity.
 - Inner tank space of the fuel storage unit on Lepse (service tanker/vessel for nuclear submarines). (Monolith for strength and contaminant immobilization).
 - In-place decommissioning of two nuclear submarine reactor compartments and associated equipment at the Russian Navy Training Center in Paldisk, Estonia. (Radiation shielding and contaminant immobilization)
- Description of in-tank waste solidification for a chemical tank using magnesium phosphate cement.

The Russian experience in aqueous waste stabilization/solidification appears to be limited. The examples discussed in the report are related to work conducted in the recent past or intended for future programs. To date, the Russians have not closed any high-level waste tanks. However, decontamination and repair of a large steel waste tank was discussed. The tank was returned to service after the repairs. In informal discussions, V. A. Starchenko stated that the Russians intend to empty and clean their high-level waste tanks and to then use them as "vaults" for storage of radioactive debris and/or packaged waste/waste forms rather than to fill the tanks with clean grout. Currently the Russians are planning for long-term storage of the low-level waste and for geologic disposal of high-level waste.

The Russian experience in decommissioning large tanks/vessels is also limited to three examples. One example involved pumping grout into the inner tank space in a Fuel Storage Unit on a tanker that serviced nuclear submarines. The concrete was a relatively high-strength concrete which was batched at a central plant and delivered to the docked tanker by truck. The concrete was pumped into the inter tank space. Approximately 6 hours was required to fill the 110 cubic meter void space.

The second example involved decommissioning two nuclear submarine reactor compartments at the Russia Navy training center in Paldisk, Estonia. Two concrete mixes

were used for "conservation" of these units. A highly fluid, pumpable concrete mix was designed for filling the compartments. This concrete also contained Shungizit porous aggregate which was intended to dissipate radiolytic gases formed in the high radiation fields associated with the inside of the reactor compartments. A concrete sarcophagi was also constructed over the reactor compartments as part of the "conservation" effort. This mix contained less cement and no porous aggregate since the radiation field was much lower.

Finally, magnesium phosphate cement was used to solidify the radioactive ferrocyanide sludge in a defective tank. The tank had a volume of 3200 cubic meters and it contained 70 cubic meters of sludge with a liquid to solid ratio of 2 to 1. The tank had no mixing capabilities so the magnesium oxide and phosphoric acid were simply added on top of the sludge. As a consequence, crust formed on top of the sludge after the first addition and precluded subsequent additions of the magnesium oxide. However, the solidification of the sludge was sufficient to stop the tank from leaking. Magnesium phosphate cement was selected for this application because of the strong stabilization/fixation properties of the resulting salts (barium, tin, zirconium and thorium phosphates are very insoluble).

The Russian regulatory requirements (in Russian) are provided in Attachment 2. These regulations have been in effect since January 1, 2001. In general the Russian requirements for cement-based waste forms are similar to the US Nuclear Regulatory Commission requirements. An abridged English summary is provided in Attachment 3, in the form of slides from a presentation on "Collecting, Reprocessing, Storage and Conditioning (Treatment) of Liquid Radioactive Waste" by V. A. Starchenko.

The Russian waste form requirements include limits on radionuclides, leaching rates, referred to as water resistance, compressive strength, radiation stability, resistance to thermal cycling and a durability requirement based on the strength of a sample immersed in water for 90 days. In addition to prohibiting waste with fire or explosive characteristics, wastes that can react with the compounds in the cement to form toxic substances such as ammonium salts are also prohibited. Complete dehydration of high-salt aqueous low-level waste solutions is prohibited per the Russian regulations in order to prevent possible exothermic interaction of the compounds in the dry residue. This sensitivity to management of dry salt waste is applicable to treatment, storage and disposal of calcined waste at DOE facilities.

Strength is used as a measure of durability and performance. Additives used to improve leaching include sodium silicate to reduce overall permeability, zeolites to improve cesium leaching and organic polymers (polymer cements including latex-modified cements) to reduce porosity/permeability and thereby improve tritium leaching. Pozzolans were discussed for improving matrix properties and alkaline additives were discussed as set regulators specifically for borate wastes.

An interesting concept employed by the Russian grout formulators is to include a porous aggregate, "Shungizit," as an ingredient in waste forms and/or decommissioning grouts exposed to high radiation doses. The purpose of the porous aggregate is to provide for gas permeability through the aggregate. In addition, the matrix portion of these grouts/waste forms is designed to have low permeability to water. This is achieved by a low water to

cement ratio in the mix. This type of mix provides a means of venting the waste form so that radiolytic gases do not accumulate while at the same time minimizing the contact between the contaminants and leachate.

The final report on Russian Grouting experience provided an opportunity for international cooperation and access to Russian grouting/waste form experience. The data on radiolytic gas generation from grout mixtures was already used in evaluation of the source of hydrogen and methane generation detected in the sampling ports around the SRS high-level waste tanks in 2002. The concept of venting the radiolytic gases from a waste form by adding porous aggregate is being considered for future cement-based TRU waste forms at SRS.

2.0 BACKGROUND

2.1 OBJECTIVE

The objectives of this work were to document the Russian experience on grouting for waste forms and tank closures or other decommissioning applications. This task was designated as Task H-4 in TFA Work Element 923, SRS TTP SR16WT51 Subtask H. The milestone designation is 923-1.5-1.

The approach for obtaining the Russian experience in ambient temperature waste treatment and in decommissioning tanks and other vessels was to issue a subcontract to the American Russian Environmental Services, Inc. (ARES) for preparation of a report on the Russian experience. ARES contracted the report to Daymos, Ltd. V. A. Starchenko from Daymos was the project manager. N. I. Alexandrov and V. P. Popik were the principal investigators. The final report from Daymos/ARES is attached.

3.0 ACKNOWLEDGEMENTS

This effort was requested and supported by L. Bustard, Sandia National Laboratory as part of the Scope of Work for the Tank Focus Area, Enhanced Grout Program.

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4.0 ATTACHMENT A

Review of the Russian Experience on Inorganic Binders for Waste Treatment and Tank Closure - Final Report

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THE REPORT

**" The Review of the Russian Experience on Inorganic
Binders for Waste Treatment and Tank Closures "**

The manager of the project
V. A . Starchenko
The responsible executors
N. I. Alexandrov
V. P. Popik

St-Petersburg 2001.

Summary.

Keywords: radioactive wastes, tanks for waste storage, radiation - dangerous objects, cementation of radioactive wastes, portland cement mixtures, radiation stability, radiolysis, radiolytical gases release, durability of the cement compositions, leaching of radionuclides, large scale experience.

In this report it is given the review of results of researches carried out in Radium Institute and in number of other Russian enterprises directed on elaboration of high-performance concrete - conserving agents designed for solidification of liquid radioactive wastes and for transfer into ecological - safe state of HAW storage tanks and decommissioned radiation - hazardous objects of nuclear power engineering. The existing Russian practical experience in the indicated area is also briefly described.

CONTENT.

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INTRODUCTION.

The present review is prepared in accordance with subcontract No 8D6266-EE/2001-01 concluded with corporation " American Russian Environmental Services, Inc." The subcontract goal is to prepare a technical report on Russian experience with the use of inorganic binders for treatment of radioactive waste and for closing of waste tanks. For reflection of the Russian experience on use of cement grouts for waste treatment and tanks closure the following major subjects were determined, which should be reflected in the report:

- research of influencing of portland cement grouts composition on the mechanical strength and radiation stability of the solidified cement mixtures;
- studies of influencing of cement grouts composition on an yield of radiolytic hydrogen at high radiation doses of compositions;
- estimation of capability to improve cement grouts at their contact with groundwater due to introducing in them of the special additives;
- estimation of capability to decrease radionuclides leaching from cement grouts due to addition of the components, which can decrease migration rate of impurities in cement matrixes;
- practical experience on application of grouting methods for decommissioning of objects of nuclear power engineering and Navy nuclear radiation hazardous facilities;
- key technical problems regarding of improvement of cement grouts properties that might be resolved through an analytical and experimental research program during the potential next stage of the project;
- filled in survey of enhanced grout needs for tank closure provided by the SRTS customer.

The compositions on the basis of ordinary portland cement (OPC) and some other inorganic binders (blast furnaces slag (BPS) and pulverized fuel ash (PFA) are broad applying for solidification of low active liquid radioactive waste (1). In Russia and in USA cement grouts are applied also to conservation of radwaste tanks and other radiation - dangerous objects. The important direction of cement grouts usage is their application as

construction materials and biological protection in containers and dry storages designed for long-term storage of burned up nuclear fuels.

For effective utilization in the mentioned above directions cement grouts should have a series of particular properties:

- high radiation stability that is especially important at usage of cement mixtures for decommissioning of objects with high level of irradiation (reactor compartments of nuclear powered vessels, burned up nuclear fuel storage);
- the structure of the cured grout should provide release of radiolytic gases without disturbance of monolith integrity;
- the structure of the cured grout should have low water permeability to ensure low leaching rate of radionuclides from the object in environment for all time of its long-term storage.

The special cement mixtures suitable for solidification of the liquid radwaste should have a following complex of properties:

- high radiation stability, that will allow to solidify radwastes with enough high level of activity;
- the structure of the cured cement mixture should have low water permeability to reduce to minimum release of the radionuclides from solidified radwastes in environment for all time of their long-term storage;
- the cured cement compositions should have high frost resistance;
- the cured cement mixtures should have low speed of leaching of the basic components of cement to provide high stability of the cured cement grout at contact with groundwater;
- the composition of cement grouts used for radwaste solidification should provide enough high mechanical strength at the high contents of soluble salts in cemented waste.

The primary goal which was put at realization of researches of cement mixtures with reference to treatment of liquid radwaste and decommissioning of radiation - hazardous objects including waste tanks was concluded in elaboration of cement mixture compositions which in the most degree satisfy to the presented above requirements.

Previously the literature on structure and properties of cured cement mixtures was studied with the purpose of selection of rational paths for

looking up of cement mixtures composition possessing a given complex of properties.

The main features of structure and properties of hardening cement mixtures with reference to problems of radwaste treatment and radiation-hazardous objects decommissioning.

The term "cement" usually implies portland cement or materials containing portland cement. The cement produces by high temperature calcination with a partial melting of materials having high content of calcium oxide. The obtained product (clinker) is crushed up to rather high specific surface (approximately $4000 \text{ cm}^2/\text{g}$) to activate cement. The cement hardening begins when this powder is mixed with water. At preparation of hardening cement mixtures the water-cement weight ratio is usually selected within the limits of 0.25-0.6; the mixtures with smaller water-cement ratio become rigid and lose plasticity whereas at the greater ratio mixtures can be stratified and liberate water. The prepared mixtures must be used within 1-2 hours then their setting starts. The development of strength becomes noticeable only in 1-2 days. Then the strength fast accrues.

In general all processes of cementation have a "window" 1-2 hours, during which the prepared mixture should be used. In further it is necessary to allow to cement to hydrate chemically without mechanical effects. The decelerators and boosters of cement setting are known, but their long-time influencing on properties of cement especially in conditions of irradiation is not enough well established and their applying for cementation of radiation - dangerous objects can not be recommended and therefore it is necessary to work with cement mixtures in the mentioned above period (I).

Internal structure of cured cement mixtures.

In structure of the cured cement it is possible to mark three characteristic features: a matrix of solid phases, both crystalline and amorphous, system of pores of the different size and form and aqueous phase located in pores. The model of a microstructure of cured cement is shown) on fig. 1.

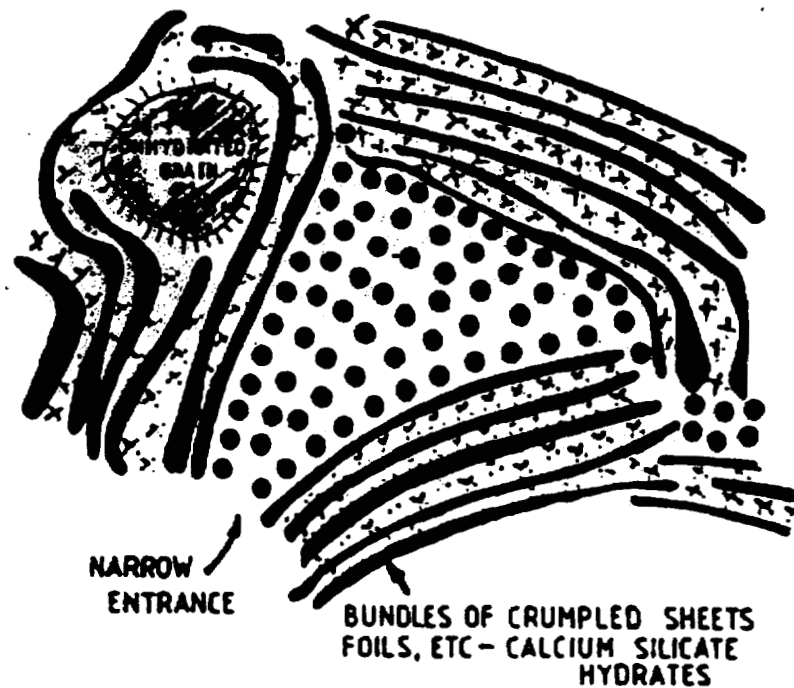


Fig. 1. Model of a microstructure of cured cement.

The gel of calcium hydrosilicate (C-S-H) is the most important component of solid phase of cured cement mixture as it contains main part of micropores. C-S-H phase is almost amorphous. As it can be seen from fig. 1, the phase of C-S-H gel consists from elements, the centers of which are grains of cement surrounded with products of its hydratation. Each element has flaky structure; the random packaging of these units creates a grid of micropores. It is not surprised that the most part of sorbtion potential of the cured cement is determined with micropores of C-S-H gel. The conducted researches show, that normally prepared samples of concrete, as a rule, do

not contain pores with size > 1 micron and the main part of pores has the size < 0.1 microns. These pores determine the diffusion characteristics of cement mixtures in relation to radioactive ions therefore measured for them diffusion constants are not property of cement matrix, but concern to system pores - matrix. It is necessary to mark that in cured cement mixtures there are also other kinds of pores. In space between hydrated and not hydrated fragments of cement so-called capillary pores are formed. These pores have large sizes than pores of C-S-H gel. Common and capillary porosity is reduced with growth of degree of cement hydration, gel porosity increases a little because the volume of C-S-H gel (2) is augmented.

C-S-H gel acts as a main factor controlling pH of cement mixtures at the greater cure period. The Ca/Si ratio in C-S-H gel varies within the limits 1.8-0.9. At Ca/Si ratio 1.8, where C-S-H gel coexists with $\text{Ca}(\text{OH})_2$, the equilibrium pH value practically equal to pH of saturated solution of calcium hydroxide. At decreasing of this ratio concentration of calcium in aqueous phase and pH are descended. The same decrease will be obtained as a result of leaching, as the cement will lose the most soluble calcium compounds. The pH of aqueous phase in pores of concrete has high importance for it properties as material for conservation of radiation-hazardous objects, since the high pH value promotes a decrease of solubility of a number of radionuclides, in particular, of most dangerous long-lived α -emitters (3) and favours to decrease of corrosion of carbon steel.

Usage of the additions for modification of properties of cement mixtures.

Addition of different components for modification of properties of cement mixtures is widely used in practice. In the table I some materials frequently added in cement are presented and the effects which are obtained with addition of such component are shown too (1).

Table I.
Materials adding in cement mixtures for improvement of their properties.

Material.	Effect from the component.
Fly ash from coal combustion.	Decrease permeability, increase mixture fluidity, lower initial heat evolution.

Ground granulated blast furnaces slag.	Decrease permeability, lower internal E_h and initial heat evolution and increase mixture fluidity.
Natural puzzolans.	Increase of sorption.
Microsilica.	Decrease permeability, increase sorption.
Superplasticizers.	Reduce water content and permeability.
$C_3A(OH)_2$, NaOH	Condition borate waste and ensure set.
Sodium silicate .	Precipitate heavy metals, decrease permeability.
Miscellaneous getters: chemical and structural.	Reduce solubility of specific radwaste species e.g. Ag^+ for iodine conditioning.
Organic polymers.	Decrease permeability, getter for tritium.

It is possible to divide materials adding in cement into three groups. One group including natural puzzolane materials, ash, microsilica and slag can be called puzzolanic because these materials are activated with cement, react with water and cement and become the integrated part of cement matrix. The size of particles of these materials are usually less a little than size of cement particles, so the formed matrix have a little more dense packing of fragments than cement matrix and provides smaller permeability. The siliceous fly ashes and slags have a high content of glass, which concerns to main puzzolanic components (4, 5). In the short term materials of this group are enough inert and more active part of mixture (cement or $C_3A(OH)_2$) determine properties of mixtures in this period.

Other materials in the table I are mainly modifying agents for matrix. The cement is usually mixed with quantity of water which is sufficient to receive fluidity of mixture appropriate to the application. But such fluidity usually receives at excess of water over that is required for a chemical hydration, it leads to porous and permeable matrix. Critical water-cement ratio indispensable for full hydration of portland cement is equal approximately 0.24, but such mixture is too hard for practical usage. The demanded fluidity can be reached at low water content by adding of superplasticizers, which are the high-molecular polar organic compounds (for example sulphonated melamin, naphthalene formaldehyde polymers or lignosulfonates(6). As usual 0.2-2 % of plasticizer, depending on it type, is diluted in mixing water. It enables to receive normal fluidity of mixtures at low water content that give possibility to obtain less permeable product. The final destiny of plasticizers in cement is not completely known. Probably initially they are fast sorbed on the products of cement hydration with the subsequent desorption and partial irreversible precipitation.

Calcium and sodium hydroxides are used for acid wastes neutralization and to condition borates which have negative influence on cement setting and even can make it impossible; addition of hydroxides reduces borates influencing.

The applying of sodium silicate is described in the literature (7), but it is not used widely in practice. This compound is soluble in water and precipitates a wide range of metallic ions from solution usually in the amorphous form, however nature of precipitations in cured cement matrixes is poorly known.

Particular getters it is offered to use to reduce leaching components of the radwastes badly sorbed by cement, for example of cesium and iodine (8). For an iodine it is offered to use addition of silver or barium (9, 10). As getter for cesium it is possible to use zeolites (II). However capacity of such components is limited because of chemical reaction between cement and zeolites. Besides the zeolite capacity is decreased because of competition of K^+ and Na^+ ions presented in cement (12). The final result of it is the necessity to add in cement of high quantity of zeolite to lower Cs^+ leaching. It results in a number of disadvantages: the mixture has high consumption of

water and low compression strength. Thus the getters application is rather specific and demands special consideration in each particular case.

The organic polymers also can be used for modification of cement matrixes. In general it is necessary to concern with caution impregnation of cement matrixes with organic polymers as the diffusion coefficients in polymers are rather high and long-term stability of polymers to irradiation and degradation under an environmental stress is either unsatisfactory or unknown. The possible advantage of polymeric -cement matrixes can be improvement of immobilization of tritium (13).

Effect of elevated temperature and radiation.

As it was noticed above, major component determining long-term properties of cured cement mixtures is C-S-H gel, which at ordinary temperatures is metastable, but exists long, natural samples of such phase with age $20 \cdot 10^5$ years (1) are known. At temperature 170-180 °C this phase crystallize in autoclave during 16-24 hours. In result of gel crystallization pH of pore liquid is decreased on 1-2 units in comparison with C-S-H gel having equivalent composition, besides a considerable change of this phase volume can take place in result of crystallization. In the literature practically there are no data on rate of crystallization of C-S-H gel at temperature below 100 °C, but it is possible to suppose that the considerable temperature rise inside of curing cement mixture is extremely undesirable because of hazard of C-S-H gel crystallization.

The information, available in the literature, demonstrates that even the high doses of absorbed γ -radiation have not negative influence on the properties of dry cement (14). The effect of irradiation on cured cement mixture is appeared basically through radiolysis of water presented in it.

Main result of water radiolysis is release of gases and, first of all, of hydrogen. Irradiation of cement mixture can also modify structure of it and increases degree of it crystallinity (15)

The yield of hydrogen at radiolysis of water in cement mixtures depends on their composition, in particular, from composition of binders, which was used at their preparation. So it was noticed that trend of hydrogen yield for mixtures in which as binders were used ordinary portland cement (OPC) and its mixture with blast furnace slag (BPS/OPC) and fly ash (PFA/OPC) is: $BPS/OPC > OPC > PFA/OPC$.

This in part may be attributed to differences of composition of aqueous solutions in pores (16).

Presented above literature information on structure and properties of cured cement mixtures allows to dedicate following main directions in elaboration of optimal composition of cement mixtures designed for radwastes treating and conservation of radiation-hazardous objects:

- usage of superplasticizers with the purpose to decrease quantity of water which is necessary for obtaining cement mixtures with demanded fluidity and low permeability;
- looking up of the addition components and filling materials ensuring to cured mixtures a gas permeability enough for deleting of radiolytical gases at preservation of their high water tightness;
- looking up of mixtures composition with a low yield of radiolytical hydrogen;
- research of possibility of using of the components sorbing radionuclides for decrease their leaching from cement mixtures.

In this report the results of experimental researches carried out in these directions are presented.

2. EXPERIMENTAL INVESTIGATION OF PROPERTIES OF SPECIAL CEMENT MIXTURES.

The main results of the carried out researches are reviewed below. In the given section of the report the techniques of experimental researches are briefly shown also. It is necessary to mark that during preliminary researches 22 cement mixtures of different composition were tested. The mixtures possessing the most favourable combination of properties were selected for further researches. The compositions of these mixtures are shown in the table 2.

Table 2.

Composition of investigated cement mixtures.

No of mixture	Main components of Mixture		Modifying Components.		Water : solid Ratio (W/S)
	Material	Content, % vol.	Material.	Content % vol.	
1.	Cement Shungizit filling	66.0 33.7	S-3 SDO	0.7 0.05	0.24

	material				
2.	Cement Shungizit filling material Shungizit sand	40.0 20.0 40.0	S-3 SDO	0.7 0.05	0.35
3.	Cement Shungizit filling material Mordernite sand	40.0 20.0 40.0	S-3 SDO	0.7 0.05	0.30
9.	Cement Quartz sand	40.0 60.0			0.38
21.	Cement Shungizit sand Clinoptilo- lite Sand Microsilica	38.0 37.0 5.0 7.0	S-3	0.9	0.32

2.1. Experimental techniques.

2.1.1. Irradiation of cement mixtures.

2.1.1.1 The characteristics of the gamma-irradiation installation.

Irradiation of investigated cement mixtures was carried out on gamma-irradiation installation of V. G. Khlopin Radium Institute, which had following basic parameters:

- Source of a gamma-radiation - Co - 60;
- Sizes of irradiation chamber:
 - height - 200 mm;
 - diameter - 120 mm;
- Calculated dose rate of gamma-radiation - 150 rad / sek.

The real dose rate in the irradiation chamber was measured with usage of chemical dosimetry method based on radiation oxidation of divalent iron ions in sulphate media saturated oxygen of air, so-called Frank's dosimeter (17).

2.1.1.2. Technique of cement mixtures irradiation.

Samples of cement mixtures were placed in glass cylindrical vessels with inner diameter and height 21-22 mm and wall thickness 1 mm or in glass ampoules with diameter 15 mm and length 90 mm with the same wall thickness. Vessels with samples of mixtures destined for research of composition and quantity of radiolytic gases were placed in titanium hermetic capsule with wall thickness 0.5 mm.

2.1.1.3. Tests of mechanical properties of cured cement mixtures.

The determination of compressive strength were carried out according to GOST 10180-90. The hydraulic press PD-10 (GOST 8905-73) was applied to tests. The inaccuracy of measurements of load did not exceed 2 % rel. Compressive strength (R_{com}) of samples was calculated according to:

$$R_{com} = F/A$$

Where: F - destructive load;

A – cross section area of sample.

The mechanical tests irradiated and not irradiated samples of the same composition were done simultaneously.

2.1.1.4. Test of cement mixtures air permeability.

The device AGAMA-2R was used for evaluation of cement mixtures air permeability. This device gave possibility to measure time which was necessary to definite volume of air pass through testing sample into evacuated chamber. As all tested samples had the identical geometrical sizes for comparison of their air permeability the value of rate of air accumulation in vacuum chamber was used.

2.1.1.5. Test of waterproof of cement mixtures.

Testing of waterproof of cured cement mixture samples was done in according to GOST 12730.5-84 on which the measure of waterproof is the water pressure (W) at which on a surface of test cylindrical sample there is no yet wet spot. The increase of water pressure was made by steps 0.2 MPa during 1-5 min After each step the stop during 16 hours was made.

2.1.1.6. Research of cement mixtures structure changes at irradiation.

For research of influencing of irradiation on structure of cement mixtures the methods X-ray phase analysis and differential thermal analysis were used.

X-ray phase analysis.

For identification of crystalline phases in investigated samples the powder method permitting to receive the information on chemical composition and structure was used. For obtaining diffraction pictures the X-ray diffractometer DRON-1,5 was used with copper anode X-ray tube at anode V = 30 kV and I = 25 mA. CuK α - radiation was filtered through Ni - foil.

The identification of crystalline phases was made by comparison of data obtained from diffractograms, with data presented in catalogue 1CPD5 issued by Integrated Committee of the Powder Diffraction Standards (USA).

Differential thermal analysis of cement mixtures.

The differential thermal analysis (DTA) of cured cement mixtures was carried out with help of derivatograph Q 1500 D of the Hungarian production.

During DTA it was fixed weight changes of grinded specimen of investigated mixtures at controlling heating from 20 to 1000°C.

2.1.1.7. Research of quantity and composition of gases which are evolving at irradiation of cement mixtures.

The chemical analysis of gas phase accumulating in capsules and ampoules during irradiation of cement mixtures was made with gas chromatographic method. The gas chromatograph "Tsvet-100" was used for gas analysis. The conditions of chromatography and system of detecting were selected recognizing that the main anticipated components of gas phase evolving at cement mixtures irradiation are: O₂, H₂, CH₄, CO₂. The accuracy of definition of the contents of these components in samples of gas was 5-10 %.

2.1.1.8. Research of leaching of radionuclides from cured cement mixtures.

Radionuclides (Pu-239, Am-241, Cs-137, Sr-90) were added in water used for cement mixtures preparation as nitrates. Before beginning of leaching experiments all specimens of cement mixtures were cured during 28 days.

The technique of experiments on definition of speed of leaching of radionuclides from hardening compositions on the basis of cement corresponded to the guidelines of IAEA (18) and GOST 2914-91 (19). The distilled water was used as leaching liquid.

The concentration of radionuclides in samples of leaching water was determined radiometrically on α -radiation for Pu-239 and Am-241, on β -radiation for Sr-90 and on γ -radiation for Cs-137. The accuracy of activity measurement of samples was 5-10 % rel.

2.2. RESULTS AND THEIR DISCUSSION.

Influencing of gamma-radiation on mechanical properties, air permeability and waterproof of cement grouts of different compositions.

As it was already marked in the introduction, primary goal of researches, the results of which are reviewed in this report, is looking up of cement mixtures (concrete) compositions which properties meet to demands to concrete - conserving agents used for conservation (closing) of radiation - hazardous objects, including waste tanks. In this connection influencing of gamma-irradiation on a mechanical strength, air permeability and waterproof of concrete of different compositions was studied. The obtained results are shown in the table 2.2.1

The table 2.2.1.

Influencing of gamma-radiation on mechanical properties, air permeability and waterproof of concrete of different compositions.

No of concrete composition	Time of curing, days	Dose of Gamma-radiation, Mrad.	Compressive strength, MPa.	Air permeability, Cm^3/sec .	Waterproof W, tm.
1	28	266	43.5	0.037	12
	90	855	41.6		
	180	1710	56.0		
	270	2565	45.9		
	690	6000	40.2		
1c	28		27.5	0.022	12
	90		25.0		
	180		20.1		
	270		29.7		

2	28	266	25.4	0.263	10
	90	855	25.0		
	180	1710	28.0		
	270	2565	26.7		
	690	6000	33.9		
2c	28		16.0	0.04	2
	90		16.8		
	180		14.7		
	270		17.4		
3	28	266	20.5	0.11	2
	90	855	21.0		
	180	1710	21.1		
	270	2565	23.8		
	690	6000	19.4		
3c	28		15.5	0.322	2
	90		15.0		
	180		13.7		
	270		16.3		
21	28	266	31.3	0.029	> 12
	90	855	34.9		
	180	1710	39.5		
	270	2565	38.8		
21c	28		37.5	0.03	> 12
	90		35.0		
	180		39.2		
	270		39.0		

As it is visible from the data of table 2.2.1., irradiation of compositions 1-3 at their curing during 28-690 day (the absorbed dose 266-6000 Mrad) results in increase of compressive strength in comparison with control samples of cement grouts curing in normal conditions (1c-3c). For composition N 21 some decrease of strength marked at curing period 28-180 days under effect of gamma-radiation, however at the greater curing period strength of sample hardening in normal conditions and under irradiation are equalized. The obtained results allow to draw a conclusion that the gamma-

irradiation of investigated compositions on the basis of portland cement with dose up to 3000 - 6000 Mrad will not render negative effect on mechanical strength of the cured compositions.

Evolution of radiolytical gases at gamma-irradiation of cement mixtures.

For definition of conditions ensuring safe long-term storage of decommissioned radiation - hazardous objects, the knowledge of composition and quantity of gases evolved at irradiation of cement mixtures used at their closure is necessary.

With this purpose two series of experiments were conducted, the goal of the first of which was estimation of composition of gases released at gamma-irradiation of cement mixtures, and the goal of the second series was determination of quantity of hydrogen evolved at irradiation of mixtures of different compositions.

The results of analysis of gas phase in titanium capsules are shown in the table 2.2.2.

The table 2.2.2.

Composition of gas phase in capsules at different radiation time.

Time, days.	Dose of Gamma- radiation, Mrad.	No of concrete compo- sition	Composition of gas phase in capsule, % vol.			
			H ₂	O ₂	CO ₂	CH ₄
0	0	1	< 0.0001	78.1	0.03	-
0	0	2	< 0.0001	78.0	0.02	-
0	0	3	< 0.0001	77.9	0.03	-
28	266.1	1	3.3	10.0	0.01	< 0.1
		2	0.1	18.6	0.1	0.02
		3	12.0	13.1	0.01	0.2
36	342.1	2	0.1	18.6	0.1	0.02
64	608.2	1	1.2	14.4	0.06	0.15
		2	0.5	11.1	0.02	0.16
		3	8.5	15.6	0.03	1.1

The results of the analysis of gas phase composition in capsules have shown that at irradiation of cement mixtures that evolution of hydrogen and

small amounts of methane take place. Evolution of hydrogen is connected with radiolysis of water containing in cement mixtures. Methane evolution is the result of radiolysis of organic components (superplasticizer S-3 and component SDO), added in mixtures during their preparation. Literature data show that methane is one of the main products of radiolysis of complex organic compounds (20). Apparently that at estimation of safety of long-term storage of radiation - hazardous objects filled with cement mixtures, it is possible to consider only hydrogen release, since quantity of other fire hazard gas - methane is insignificant.

For more reliable determination of hydrogen quantity released at gamma-irradiation of cement mixtures, the experiments on their irradiation in soldered glass ampoules were done that eliminated a capability of leakage of gases during irradiation. The obtained results are shown in table 2.2.3.

The table 2.2.3.

Evolution of radiolytic hydrogen at irradiation cement mixtures in glass ampoules.

No of concrete composition	Irradiation time, days.	Dose of Gamma-radiation, Mrad.	Hydrogen evolution rate, l/m ³ of mixture per hour.
1	5	47.5	0.018
	15	142.6	0.106
	29	275.6	0.064
2	5	47.5	0.034
	15	142.6	0.012
	29	275.6	0.058
9	5	47.5	0.025
	15	142.6	0.01
	29	275.6	0.01

As it is visible from the data of the table 2.2.3. the rate of hydrogen evolution does not exceed 0.11 l / m³ of mixture per hour at dose rate 110 rad / sek. Apparently that the evolution of radiolytical hydrogen is necessary to take into account as the dangerous factor only at conservation with the help of cement mixtures of objects with high radiation level.

Research of influencing of addition of boron carbide on release of radiolytical hydrogen from cement mixture at irradiation.

At concreting of the objects containing fissile materials for maintenance of nuclear safety it can be necessary to add in cement mixtures used for their conservation matters – neutron poisons. One of the most known matters of such type is the carbide of boron - SiC. In this connection the experiments on influencing of addition of SiC in mixture No 2 on radiolytical hydrogen release were made. With this purpose the irradiation of mixture No 2 with addition of SiC in soldered ampoules was made. The powder of SiC in quantity 50 g/kg of cement mixture was added in dry mixture of components of composition No 2 before mixing with water.

The results of determination of quantity of radiolytical hydrogen evolved at irradiation of composition No 2 without and with addition of SiC presented in table 2.2.4.

The table 2.2.4.

Influencing of addition of SiC on evolution of hydrogen at irradiation of composition No 2.

Irradiated Composition	Weight of composition in ampoule, g.	Irradiation time, days.	Dose of Gamma-radiation, Mrad.	Hydrogen Evolution rate, L/m ³ of mixture per hour.
No2	12.3	5	47.5	0.034
	14.6	15	142.6	0.012
	10.0	29	275.6	0.052
No2 + SiC	10.7	7	66.5	0.028
	12.5	28	266.1	0.051
	12.7	70	665.3	0.053

As it is visible from the data of the table 2.2.4, the introducing of SiC in composition of cement mixture practically has not effect on rate of hydrogen evolution at gamma-irradiation of mixture.

Determination of quantity of radiolytical hydrogen which is held back by concrete.

At irradiation of compositions on the basis of cement radiolytic hydrogen is generating inside cement mixture and than goes out from mixture

by diffusion through a system of cement mixture pores. It was possible to expect that the part of radiolytical hydrogen will remain in mixture phase. In this connection the research of content of hydrogen in samples of the irradiated cement mixtures was carry out.

The results of experiments on definition of hydrogen contents in samples of mixtures having compositions No 1, 2 and 3, irradiated 90 days (gamma-radiation dose 855 Mrad), are presented in the table 2.2.5.

Table 2.2.5.
The residual contents of hydrogen in samples
of irradiated compositions.

Temperature of Mixture Heating, °C.	No of composition					
	1		2		3	
	Quantity of H ₂		Quantity of H ₂		Quantity of H ₂	
	% from com-mon.	l/t of mixture.	% from com-mon.	l/t of mixture.	% from com-mon.	l/t of mixture.
200	1.0	0.3	3.0	1.4	-	-
250	-	-	-	-	3.0	0.4
400	67.0	18.3	65.0	31.4	-	-
500	99.0	26.9	100.0	48.4	37.0	5.3
700	100.0	27.1	-	-	96.0	13.9
900	-	-	-	-	100.0	14.5

From the data, presented in the table 2.2.5, it is visible that all studied samples of the irradiated mixtures are containing significant amounts of hydrogen, and at heating the output of the main quantity of hydrogen is occurred at temperature 400 -500 °C for mixtures 1 and 2 and 500-700 °C for mixture 3. The fact that at temperature 200-250 °C the output of hydrogen is a little indicates that the binding strength of hydrogen with cement matrix is higher than at it physical adsorption. The data of the table 2.2.5 allow to suppose that the main part of hydrogen leaves from mixture at temperature at which destruction of crystallohydrates obtained at hydration of cement takes place. These crystallohydrates can retain hydrogen by formation of solid solutions similarly to chalkstone (21). Probably also holding of hydrogen by samples because of it including into closed micropores (22).

Research of influencing of the additives on leaching rate of radionuclides.

The results of experiments on influencing of addition into cement mixtures of matters which are capable to sorb radionuclides, on rate of their leaching are shown in the table 2.2.6.

The table 2.2.6.

Influencing of the addition of sorbents on leaching rate of Cs-137 and Sr-90 from cement mixtures.

Leaching time, days.	Total fraction of a leached radionuclide, % from initial quantity.							
	Composition I		Composition II		Composition III		Composition IV	
	Cs-137	Sr-90	Cs-137	Sr-90	Cs-137	Sr-90	Cs-137	Sr-90
1	0.05	<0.01	<0.01	0.15	0.26	<0.01	<0.01	0.11
4	0.18	<0.01	0.05	0.15	0.75	0.44	0.08	0.15
7	0.24	<0.01	0.12	0.28	0.92	0.72	0.08	0.19
13	0.50	<0.01	0.16	0.28	1.29	0.80	0.08	0.27
26	0.80	<0.01	0.16	0.28	2.28	0.84	0.08	0.33

The matters added to cement mixtures were:

- composition I – without addition;
- composition II – natural zeolite – clinoptilolite;
- composition III- antimony phosphate;
- composition IV- tin phosphate.

The selection of these inorganic sorbents was determined by that they are capable effectively to sorb radionuclides from solutions of miscellaneous compositions, including solutions, close on composition to pore solutions of cured cement mixtures (23, 24, 25).

As it is visible from the data of the table 2.2.6, the addition in cement mixture of the mentioned above components has essential influencing on leaching rates of Cs-137 and Sr-90.

The introducing in cement mixture of 10 % of clinoptilolite and tin phosphate results in decrease of fraction Cs-137 leached during 26 day in 5 and 10 times accordingly. The addition of antimony phosphate lead to increase of Cs-137 leaching.

In the case of Sr-90 the minimum leaching rate is watched for cement mixture without any additives, the introducing in a structure of composition

any of the tested components results in increase of leaching rate, which is most significant in case of addition of antimony phosphate.

The results of the carried out researches have shown that the addition in cement mixtures of matters which are capable to sorb radionuclides, can reduce their leaching. However, the influencing of such components on properties of cured cement mixtures has complex nature and in some cases can result not in decrease, but even in increase of leaching rate which can be connected with negative effect of additives on structure of cured cement mixtures.

The results of done researches have shown that the composition of portland cement mixtures has high influence on properties of these mixtures. Changing composition of cement mixtures it is possible to obtain mixtures possessing complex of properties in the most degree adequate to areas of their applying.

In the present review we consider two fields of application of portland cement mixtures:

- conservation (closure) of radiation - hazardous objects of atomic engineering, in particular of waste tanks, reactor compartments of vessels with nuclear energy installations etc.;
- solidification and preparing for long-term storage of the liquid radwastes.

The optimal complex of properties of cement mixtures designed for applying in each of introduced above areas can be various.

So at usage of these mixtures for conservation of radiation - hazardous objects with high radiation level the important value has a high gas permeability of using mixtures because that allows to ensure going out of radiolytical gases without disturbance of concrete monolith integrity. For cement mixtures intended for solidification of the liquid radwastes middle and low level of activity the requirements of low leaching rate of radionuclides and high stability of mixture at affect of groundwater and other factors of environment of radwastes storage are going on the foreground.

Considering from these positions results of researches of portland cement mixtures it is possible to make following conclusions.

For conservation (closure) of radiation-hazardous objects with high level of radiation for which the release of significant amount of radiolytical hydrogen is possible, the most favourable combination of properties has the

composition No 2, as it has a high gas permeability, that provides output of hydrogen from massive of the cured composition without disturbance of its integrity.

For conservation of radiation-hazardous objects with low radiation level, for which quantity of emanation of radiolytical hydrogen is insignificant, and for solidification of the liquid radwastes the preference is necessary to give to composition No 21, which has a low permeability, low rate of radionuclides leaching and highest stability to affect of groundwater from studied compositions on the basis of portland cement

Evaluation of service time of the cured cement mixtures at long-term storage under affect of gamma-radiation and factors of environment.

The different factors of an environment of storage act on the cured compositions utilized for conservation of radiation-hazardous objects or for cementation of radwastes prepared to long-term storage. These factors cause corrosion of cement mixtures that results in decreasing of their durability. As the cured compositions should ensure safe long-term storage of radiation-hazardous objects and cemented radwastes it is important to have a capability of the evaluation of durability of cement mixtures in conditions of their storage.

For estimation of demanded service time of the cured cement mixtures which is necessary for ecological safe handling with conservated (closed) radiation-hazardous objects and cemented radwastes it is possible to start with following reasons.

The radionuclides which can be contained in radiation-hazardous objects and radwastes can be divided into three groups

- short-lived nuclides with a half-life up to 2-3 years;
- the long-lived fission products, basic of which are Cs-137 and Sr-90, having a half-life about 30 years;
- superlong-lived nuclides (actinides, Pd-107, Tc-99, I-129) the half-life of which reaches hundreds thousand and even millions years.

For nuclides of the first group for their practically full disintegration it is enough several tens years and the reliability of cement mixtures on this period does not cause doubts.

For nuclides of the second group for practically full disintegration (the decrease of activity in 100 000 times) it is necessary time about 500 years.

Nuclides of the third group for their disintegration need time measured in millions of years that far leaves the frameworks of the most optimistic estimations of durability of the cured mixtures on the base of portland cement.

Outgoing from above-stated, is reasonable to esteem cementation with mixtures on the basis of portland cement as reasonable method for maintenance of safe storage of the radwastes containing nuclides of the first and the second groups for it is necessary that the durability of mixtures was not less than 500 years. Apparently, that for estimation of suitability cement mixtures for this purpose it is desirable to have possibility to predict their durability in conditions of affect on them of gamma-radiation and storage environment.

The analysis of reasons which can lead to decrease of strength and impairment of other physicochemical properties of concretes has shown that *the primary one is the* interaction with groundwater and temperature regime of storage. The negative influencing on durability of concrete can be done also by irradiation, but this factor can become essential only for objects with high level of radiation (absorbed dose more than 2000 Mrad).

Interaction with groundwater leads to leaching from concrete dissoluble calcium compounds that results in change of structure of solid phases of cement matrix and, as consequent of it, to decrease of strength and change of other physicochemical properties of concrete. Besides the contact with groundwater is a reason of leaching of radionuclides from cement matrixes.

The negative influencing on durability of concrete can render also periodic cooling it up to temperature at which freezing a liquid in pores of cement matrix can take place that can lead to development of microcracks in structure of concrete that results in decrease of it strength, acceleration of leaching of components which are included in structure of concrete and radionuclides too. This factor may be important when the cemented objects are stored without weather protection in climatic conditions in which in winter period the probably long-lived temperature fall is lower $-18-20^{\circ}\text{C}$. Such situation is represented rather improbable. Besides the conducted special researches have shown that designed cement mixtures have the class of frost

resistance not below $F=300$ according to GOST 10060-87 that guarantees preservation of properties of concrete on predictable period.

Thus as the main factor determining durability of concrete, used for conservation of radiation-hazardous objects, including waste tanks, and for solidification of the liquid radwastes, it is necessary to consider interaction of concretes with groundwater.

As a parameter of properties of concrete at estimation of their durability was chosen their compression strength because the change of this parameter mirrors changes happening in structure of concrete.

Corrosion of the cured cement mixtures at interaction with groundwater.

At contact of the cured cement mixtures with groundwater the leaching of $\text{Ca}(\text{OH})_2$ takes place, rate of which is limited by Ca^{+2} diffusion through system of matrix - pores of cement mixture.

For estimation of service time of the cured mixtures on the basis of cement it is necessary to have the information on leaching rate of calcium from it. The data on leaching rate of calcium from mixtures No 2 and 21 are shown in the table 2.2.7.

Table 2.2.7.

Leaching rate of calcium from mixtures No 2 and 21.

No of composition	Time of leaching, days	Total fraction of leached $\text{Ca}(\text{OH})_2$
2	3	0.0144
	6	0.0203
	10	0.00263
	20	0.00371
	30	0.00456
	40	0.00526
	50	0.00589
21	60	0.00645
	3	0.000181
	6	0.000235
	10	0.00033

	20	0.000465
	30	0.000572
	40	0.00066
	50	0.000738
	60	0.00081

The diffusion coefficients of calcium in mixtures No 2 and 21, calculated on the basis of the data of table 2.2.7. are equal:

For mixture No 2 - $3.1 \cdot 10^{-15} \text{ m}^2/\text{sec}$;

For mixture No 21 - $3.8 \cdot 10^{-16} \text{ m}^2/\text{sec}$

These values of a diffusion coefficients of calcium in mixtures No 2 and 21 were used for estimation of service time of these mixtures at a contact with groundwater.

. For calculation of speed of leaching C_a it is accepted:

- the package with the cemented radwaste has the form of barrels with diameter 1 m which are located in storage as a dense packing thus the volume of groundwater directly interacting with composition is equal to $0.215 \text{ m}^3/\text{m}^3$ of cement mixture;
- the leaching rate of C_a depends on speed of groundwater current in storage therefore calculations were made for three speeds of water current : 1, 10, and 100 m / years;
- for calculation of C_a leaching rate it was adopted the model, according to which the cylindrical units of cement mixtures are completely filled up with groundwater, which is contacting with mixture definite time dependent on speed of water current in storage then it is substituted on a fresh portion of groundwater and the procedure repeats;
- the concentration of C_a in groundwater is small in comparison with it concentration in pores of cement mixture that corresponds to maximum rate of Ca leaching from mixture.

The solution of a diffusion equation for this case are known (25). In the table 2.2.8. service time of mixtures No 2 and 21 calculated on the basis of above presented reasons are shown.

Table 2.2.8.

Calculated service time of compositions N 2 and 21 at different speeds of water current in storage of cemented radwaste .
(The packages of cemented radwaste have the form of barrels with diameter 1 m).

No of composition	Speed of water current , m / year	Service time of composition, years
2	1	$2.5 \cdot 10^3$
	10	$7.9 \cdot 10^2$
	100	$2.5 \cdot 10^2$
21	1	$7.0 \cdot 10^3$
	10	$2.2 \cdot 10^3$
	100	$7.0 \cdot 10^2$

As it is visible from the table 2.2.8., estimated service time of composition N 2 at speed of groundwater current in storage of radwastes up to 10 m / years will exceed demanded value 500 years, however at more high speed of groundwater in storage it stability to calcium leaching can be not enough to guarantee safe storage of the cemented radwastes on given term. Considerably best parameters has the composition No 21 for which even at speed of groundwater current 100 m / years calculated service time is 700 years, that notably exceeds time (500 years) of radwastes storage containing Cs-137 and Sr-90, demanded for practically full decay of these radionuclides.

Research of cementation of simulated radioactive pulps on MCC.

The researches on usage of cementation for solidification of radioactive pulps was made on Mining-Chemical-Combine. The portland cement M 400 was used in these researches. Permissible quantity of pulps entered in cement mixture is determined, which allows to obtain the cured cement grout corresponding to the Russian requirements (RD 9510497-93 "Quality of compounds, obtained at cementation of low and middle active liquid radioactive wastes. Specifications. MINATOM of Russian Federation, 1993).

The Main results of carried out researches are presented below.

In the table 2.2.9 the data on influence of quantity of the pulp entered into cement mixture on strength of cured mixture are shown. 10 % of bentonite from weight of cement was entered into cement mixture as the component for decreasing of leaching rates of radionuclides from cured cement mixtures..

The table 2.2.9
Influencing of quantity of pulp on strength of cured cement mixtures.

Composition of cement mixture.			Weight water/ cement ratio	Compressive Strength, MPa
Cement / Bentonite ratio	The contents, % weight.			
	Cement + Bentonite	Pulp		
10:0	100	0	0.7	18.0
9:1	100	0	1.0	14.5
9:1	90	10	1.0	17.0
9:1	80	20	1.0	18.0
9:1	70	30	1.0	13.0
9:1	60	40	1.0	3.0
9:1	20	80	1.0	1.0

The data, showed in the table 1, demonstrate that satisfactory compression strength, equal to 13 MPa, have samples of cured cement mixtures containing up to 30 % weight of pulp. Increasing of content of pulp in cement mixture above this limit leads to sharp decreasing of compressive strength and these mixtures does not fulfil conditions of the Russian standards of safety (RD 9510497-93).

The conducted researches have allowed to recommend for solidification of radioactive pulps the following composition of cement mixture:

- binding – portland cement M400;
- bentonite - 10 % from weight of cement;
- radioactive pulp- about 30 % from weight of cement;
- water/cement ratio 1: 1.

The leaching rate of Cs-137 and Pu-239 was studied for cement mixtures, compositions of which are shown in the table 2.2.10

The table 2.2.10

Composition of cement mixtures for research of leaching rate of Cs-137 and Pu-239.

N Of sam ple	Composition of cement mixtures, weight %						
	Cem- ent	Bento- nite	Clino- ptilolite	Rad- waste pulp	Water/ cement ratio	Radio- nuclide	Activity Ci/kg
1	100	-	-	35	1.0	Cs-137	2.0x10-3
2	90	10	-	33	1.1	Cs-137	1.8x10-3
3	95	5	-	34	1.1	Cs-137	1.9x10-3
4*	91	9	-	33	1.0	Cs-137	1.8x10-3
5	91	-	9	33	1.0	Cs-137	1.8x10-3
6	100	-	-	35	1.0	Pu-239	1.3x10-2
7	91	9	-	33	1.1	Pu-239	1.3x10-2
8*	91	9	-	33	1.0	Pu-239	1.2x10-2

The notice - * in samples 4 and 8 the bentonite dried up to constant weight at temperature 100 °C was added.

The data on leaching rate of Cs-137 and Pu-239 from investigated cement mixtures are presented in the tables 2.2.11 and 2.2.12.

The table 2.2.11.

Leaching rate of Cs-137 from cement mixtures (composition of samples presented in table 2.2.10).

Contact time of sample with water, days.	Leaching rate of Cs-137 from samples of cement mixtures, g/sm ² xday				
	1	2	3	4	5
15	8.5×10^{-3}	1.3×10^{-3}	3.1×10^{-3}	1.6×10^{-4}	1.6×10^{-3}
28	5.1×10^{-3}	8.8×10^{-4}	1.8×10^{-3}	8.0×10^{-5}	5.0×10^{-4}
58	2.6×10^{-3}	4.1×10^{-4}	8.2×10^{-4}	3.0×10^{-5}	-
150	2.0×10^{-3}	8.5×10^{-4}	3.8×10^{-4}	8.0×10^{-5}	-
190	1.0×10^{-3}	1.3×10^{-4}	-	2.5×10^{-5}	-
265	1.0×10^{-3}	1.0×10^{-4}	-	1.0×10^{-5}	-
350	1.0×10^{-3}	-	-	-	-

The table 2.2.12

Rate of Pu-239 leaching from cement mixtures
(composition of samples presented in table 2.2.10).

Contact time of sample with water, days.	Rate of Pu—239 leaching from samples of cement mixtures, g/sm ² xday.		
	6	7	8
15	9.2×10^{-5}	3.3×10^{-5}	1.0×10^{-5}
48	2.1×10^{-5}	1.0×10^{-5}	4.0×10^{-7}
140	2.0×10^{-7}	2.0×10^{-7}	1.0×10^{-7}

The results of the carried out experiments have shown that the addition of clinoptilolite and bentonite, especially bentonite dried up to constant weight at 100 °C, essentially decreases leaching rate of Cs-137 from cement mixtures. In case of plutonium the influencing of bentonite addition on leaching rate is not so significant.

The experiments, results of which presented above, were carried out without exchange of contact solution that imitated emergency submergence of radwastes storage.

Magnesium-phosphate cement for solidification of the liquid radwastes and pulps directly in waste tanks.

In a number of cases there is a necessity of solidification of the liquid radwastes or radioactive pulps directly in waste tanks in which the stirring is very difficult or is impossible. The carried out researches have shown that for this purpose it is perspective to use cements on the phosphate basis which is forming at interaction of phosphoric acid with compounds of different metals, in particular with caustic magnesite.

In work /27/ the main positions reflecting influence of chemical composition of phosphate compounds on capability and on conditions of development of astringent properties were formulated:

1. The phosphate cements are received at interaction of phosphoric acid with powdery materials (oxides, hydroxides, phosphates etc.) in broad range of their composition.
2. The intensity of development of astringent properties in system " oxide - phosphoric acid " is objective function of value of ionic potential (relation of a charge to effective radius) cation of oxide.
3. The major factor determining a capability of obtaining of phosphate cement is the right selection of ratio of reaction rate of phosphoric acid with oxide (generation rate of germs of crystals) and speed of gelation of cement.

Application of cements of phosphate solidification for an immobilization of radioactive waste is perspective from the point of view of strong fixation of radionuclides in structure of cement mixture. The large group of mineral ion exchangers is known on the basis of indissoluble salts of phosphoric acids

/28/, such as phosphates of barium, tin, zirconium, thorium etc., which effectively retain different radionuclides. It gives the basis to guess that after immobilization of radioactive waste in phosphate cement there will be a strong fixation of radionuclides.

On the basis of above-stated it was offered technique /28/ of solidification of liquid radioactive wastes with applying as binding of magnesium-phosphate cement.

In according to this technique in radioactive waste the concentrated orthophosphoric acid and caustic magnesite must be sequentially added at weight ratio radwaste pulp: orthophosphoric acid: caustic magnesite equal to 1:0,3:0,5 accordingly. After that the mixture is maintained during time which is necessary for solidification. The plant tests /30/ on solidification of 70 m³ of radioactive ferrocyanide pulp directly in defective radwaste storage tank - AG - 8301/1 having volume 3200 m³ at radiochemical plant MCC was made. On technological calculations for solidification of 70 m³ of pulp having ratio solid to liquid phase equal 1:2, it was required 25,8 t of concentrated phosphoric acid and 42 t of caustic magnesite. The distinctive feature of technological process of solidification was that in the tank the system of mixing was absent that complicated process of solidification. As a result of it, after supply in the tank of all quantity of phosphoric acid and the first portion (3,5 tons) of caustic magnesite the dense layer of magnesium-phosphate cement was formed on the surface of pulp that precluded entry of caustic magnesite into mixture of pulp and phosphoric acid and because of that has not given capability to finish process of solidification.

In laboratory conditions the researches were carried out to choice the conditions of the introducing in waste tank of phosphoric acid and caustic magnesite which would give a capability to make solidification in all volume of waste. The results of these experiments show that for this purpose it is necessary:

- concentration of phosphoric acid in waste must be 90-106 g/l;
- all demanded quantity of caustic magnesite should be entered in one portion during possible short time;
- after the addition of magnesite the system must be stayed during 100 day for solidification of the formed cement.

In accordance with recommendations prepared on the basis of results of laboratory researches, the following technological decisions were adopted:

- to add in tank calculated quantity of water for decreasing of density of aqueous phase of pulp from 1.412 g/sm^3 to 1.32 g/sm^3 and decreasing of phosphoric acid concentration from 196 g/l up to 106 g/l;
- the addition of all demanded quantity of magnesite carry out in one portion during possible short time;
- after magnesite addition to add in tank 1.5 t of phosphoric acid to guarantee obtaining of magnesium-phosphate cement on the surface of waste.

After carrying out of all these operations reaction mixture in tank was stored during 100 days. The samples, which were taken after that, showed that magnesium-phosphate cement monolith was formed in whole volume of radwaste in tank.

The carried out works have allowed to solidificate 70 m^3 of radioactive pulp that gave possibility to localize radionuclides in cured cement mixture and to eliminate leakage of radionuclides from defective tank in ground waters.

The installations for cementation of radioactive wastes developed in Russian Federation.

The method of cementation is considered in Russian Federation now as the main method for reprocessing of low and middle active radwastes. In this connection the significant attention in Russia was paid to developing of equipment for this purpose

To the present time the number of such installations is designed, the brief description and the characteristics of which are presented below.

1. Installation of cementation on RTP "ATOMFLOT".

The installation is designed for cementation of radioactive wastes which are obtained at exploitation of atomic-powered icebreakers.

The radwastes of different chemical and phase composition can be processed on this installation:

- saline solutions including brines and concentrate from the installation of membrane cleaning;

- hydroxide pulps;
- pulps of inorganic sorbents.

Cement mixtures obtained on the installation, are packaged in protective concrete containers UNZK-150-1.5P with capacity 1.5 m³. Activity of cement mixtures must be not more than 6×10^{-3} Ci/kg.

Structure of the installation.

The installation consists of five blocks:

- system of cement feed in the block of mixture preparation;
- system of radwastes preparing and its feed in the block of cement mixture preparation;
- block of cement mixtures preparation and discharging of it in the container;
- system of containers transportation;
- the control system.

Characteristics of the installation.

1.	Concentration of salts in radwaste solutions, g/l	Up to 200
2.	pH of solutions	7 - 10
3.	Specific activity of solution, Bq/l	Up to 1.86×10^7
4.	Concentration of solid phase in pulp, g/l	Up to 200
5.	Specific activity of pulp, Bq/l	Up to 2.22×10^8
6.	Consumption of cement, kg/hour	600-1200
7.	Consumption of the additions, kg/hour	60-120
8.	Consumption of compressed air (6 atm.), kg/hour	Up to 50
9.	Yield of waste gases, kg/hour	Up to 60
10.	Specific activity of overflow gases, Bq/m ³	Not more than 3.7
11.	Weight water-cement ratio	0.4-0.7
12.	Weight fraction of salts in cement mixture, %	Not less than 7
13.	Weight fraction of pulps solid phase in cement mixture, %	7-8.5
14.	Degree of the container filling, %	Not less than 85
15.	Consumed electrical power	No more than 32.5 kw
16.	Temperature of air at exploitation	5 - 40 °C

2. Installation for cementation of the ash from incineration of combustible solid radwastes on Smolensk Nuclear Power Plant..

The installation of cementation is designed for cementation of the ash which is obtained at incineration of solid combustible radioactive wastes. It

contains up to 99 % of radionuclides from their quantity in an initial combustible solid radioactive waste.

The installation includes:

- bunker for cement;
- vessel for water;
- vessel for collecting of ash with volume 200 l;
- the automotive protective container;
- auger feeder for ash;
- feeder for batching of cement;
- unit for mixing of ash, cement and water.

Characteristics of the installation.

Filled with ash the barrel located in the automotive protective container, goes on the installation of cementation.. The barrel with ash is connected to the cover having the electric drive with mixer and admissions for cement and water.

The cement feeds from bunker with portions up to 70 kg.

The water feeds from vessel with portions up to 70 l.

The consumption of cement - 0.6 - 1.0 kg / hour.

Quantity of cement compound - 1.6 - 2.6 kg / hour.

Specific activity of cement compound - up to 1×10^{-2} Ci/kg.

3. Installation of cementation liquid radwastes in building 101

NITI.

The installation is designed for cementation of liquid radwaste concentrates. The solidification is made directly inside primary packaging (barrel).

The installation can be utilized on objects, on which the volume and regularity of liquid radwastes formation make stationary installation economically inexpedient.

The portland cement M500 (GOST 10178-85) will be used for cementation of liquid radwaste concentrates. The different synthetic and natural inorganic sorbents (nickel ferrocyanide on silicogel (NGA- "Celeks - CFN" TU 95-2385-92, bentonite clay (GOST 7032-75), clinoptilolite,

vermiculite etc.) in quantity 5-15 % from weight of cement can be applied as sorbing additives.

The modular design is adopted for installation that allows to convey it on different objects.

Characteristics of the installation.

1.	Installation capacity: - on concentrate of liquid radwastes , m ³ /year - on cement compound, m ³ /year:	100 Up to 142
2.	Concentration of salts in radwaste solutions, g/l	Up to 200
3.	Quantity of components on cementation of one barrel: - concentrate of liquid radwastes , l - cement, kg - sorbing components, kg	126 180 10
4.	Weight of barrel with cement compound, kg	Up to 350
5.	Specific weight of cement compound, kg / l	1.8-2.0
6.	Volume of barrel with cement compound, l	200
7.	Radiochemical composition of liquid radwastes	Co-60, Sr-90, Cs-137
8.	Average chemical composition of liquid radwaste concentrates :	
	HCO ₃	25-35 %
	Cl ⁻	18-25 %
	SO ₄ -2	10-15 %
	NO ₃ -	1-2 %
	Ca+2	8-12 %
	Mg+2	1-5 %
	Na +	8-12 %
	K +	4-8 %
	NH ₄ +	0.1-0.3 %
	Fe+3	1-3 %
	Petroleum	1.5 %?
	PH	6.5-8.5
	Density, g/l	1.045
9.	Specific activity of liquid radwastes concentrate , Ci/l	1x10 ⁻⁵
10.	Consumed electrical power, kw	Up to 5
11.	Operational mode of the installation	Periodic
12.	The design of installation	Modular
13.	Quantity of modules at transportation	2
14.	Overall dimensions, mm	
	Module 1	3500x1350x2000
	Module 2	3500x2600x2000
15.	Weight of the installation (net), kg	
	Module 1	1000
	Module 2	2000

4. Installation for cementation radwastes on Moscow NPO "Radon".

The modular installation of cementation with the vortex mixer designed for processing of liquid radwastes concentrates, pulp of ion-exchange resins and inorganic sorbents.

Cement compound obtained on the installation with activity not more than 5×10^{-4} Ci/kg is packaging in steel barrels with volume 200 l.

The installation consists of following modules:

- preparation of cement mixture;
- transport;
- preparation of pulps;
- preparation of inorganic sorbents ;
- preparation of ionexchange resins;
- pumps-batchers;
- ventilation;
- control panel;
- electric switchboard.

Characteristics of the installation.

1.	Capacity on cement grout, m ³ /hour	1.5
2.	Capacity on liquid radwastes (at (water/cement ratio – 0.75), m ³ /hour	1.0
3.	Concentration of salts in radwaste concentrates , g/l	Up to 1000
4.	Cementing material	Portland cement M400 and M500
5.	Density of cement grout, kg / l	1.5-2.2
6.	Rate of Cs-137 leaching, g/ sm ² xday	$2 \times 10^{-3} - 4 \times 10^{-6}$
7.	The sorbing additives	Bentonite, natural zeolites
8.	Quantity of the sorbing additives, % of weight of cement grout	1 – 5 %
9.	Quantity of superplasticizer, % of weight of cement grout	0.1 – 1.0 %
10.	Water/cement ratio	0.4 - 0.8
11.	Specific activity of reprocessed solutions, Ci/l	Up to 1×10^{-3}
12.	Operational mode	Periodic or continuous
13.	Process control	Manual or automatic
14.	Primary packaging	Steel barrel V=200 l

15.	Service life of the installation, years	Not less than 10
16.	Total mass, metric ton	27
17.	Consumed electrical power, kw	150

The modular installation of cementation with the vortex mixer provides high quality of cement grout, has capability of fast change of its structure depending on kind of reprocessed radioactive waste, allows to reprocess waste with the considerable contents of solid suspended matters and enables to lower quantity of secondary waste (decontamination water used for washing of the mixing chamber).

5. Installation of cementation of liquid radioactive waste "ATOMmash".

The modular installation of cementation is designed for solidification of concentrates obtained at evaporation of liquid radwastes, pulps of filtering materials and liquid organic waste of low activity level.

Cement grout with specific activity no more than 1×10^{-4} Ci/kg obtained on the installation is packaged in steel barrels with volume 200 l.

Characteristics of the installation.

1.	Capacity on cement grout, m ³ /hour	1.0
3.	Concentration of salts in radwaste concentrates, g/l	Up to 200
4.	Cementing material	Portland cement M400 and M500
5.	Density of cement grout, kg / l	1.5-2.2
6.	The sorbing additives	Bentonite, natural zeolites
7.	Quantity of the sorbing additives, % of weight of cement grout	1 – 5 %
8.	Quantity of superplasticizer, % of weight of cement grout	0.1 – 1.0 %
9.	Water/cement ratio	0.4 - 0.8
10.	Specific activity of reprocessed solutions, Ci/l	Up to 5×10^{-4}
11.	Operational mode	Periodic or continuous
12.	Process control	Manual or automatic
13.	Primary packaging	Steel barrel V=200 l

In conclusion the basic characteristics of the installations of cementation designed in Russia are presented below.

Basic characteristics of the Russian installations of cementation.

The characteristics of the installations	Place of location of the installation				
	RTP "ATOMFLOT"	Smolensk NPP	RNC "NITI"	Moscow SPA "RADON"	ATOMmash
Composition of the cemented radwastes	Liquid radwastes with salt content up to 200 g/l, hydroxide pulps and pulps of inorganic sorbents	Ash from incineration of combustible solid radwastes.	Liquid radwastes with salt content up to 200 g/l, pulp of ion-exchange resins and inorganic sorbents	Liquid radwastes with salt content up to 1000 g/l, pulps of ion-exchange resins and inorganic sorbents	Residues from evaporation of liquid radwastes, pulps of filtrating materials, liquid organic Low level radwastes
Capacity on cement - grout	Up to 1.0 m ³ /hour	Up to 2.6 Kg / hour	Till 0.13 m ³ /hour	Up to 1.5 m ³ /hour	Up to 1.3 m ³ /hour
Specific activity of cement grout, Ci/kg	Up to 6x10 ⁻³	Up to 1.0x10 ⁻²	Up to 1.0x10 ⁻⁵	Up to 5x10 ⁻⁴	Up to 4x10 ⁻⁴
Type of cement grout package	The protective concrete container UNZK-150-1.5P	Steel barrel V=200 l	Steel barrel V=200 l	Steel barrel V=200 l	Steel barrel V=200 l
Design features of the installation	Fixed location in building with radiation protection.	Fixed location in building with radiation protection.	The modular installation	The modular installation	The modular installation
Development stage	Installation is mounted on RTP "ATOMFLOT" and now is in industrial testing	The working documentation is designed and confirmed by regulatory authorities.	The cold tests of experimental Installation was carried out	Installation is mounted on Moscow NPO "RADON" and now is in industrial exploitation	The working documentation is designed and confirmed by regulatory authorities.
Enterprise-Designer	SverdNIIchim-mash	GI VNIPIET	RNC "NITI"	Moscow NPO "RADON"	"ATOMMASH"

3. LARGE SCALE EXPERIENCE OF APPLICATION OF CEMENTATION METHODS FOR CONSERVATION OF RADIATION-HAZARDOUS OBJECTS IN RUSSIA.

Up to the present time in Russia there is no experience on applying of cementation for conservation (closure) of waste tanks. It is connected with that waste tanks in which the main part of the accumulated radwastes is

stored in Russia manufactured from corrosion-resistant stainless steel that reduces to minimum hazard of affect of these wastes on environment.

The radiation-hazardous objects of nuclear fleet removed from exploitation have significantly larger hazard to environment therefore on conservation of these objects it is paid prime attention now.

To the present time the large scale works on conservation of two objects of nuclear fleet were made:

- floating technical base "Lepse" (ship assigned to maintenance of atomic ice breakers) of Murmansk marine shipping company;
- two reactor compartments of nuclear submarines in former training center of the Russian Navy in Paldisk Estonia.

1. Cementation of intertank space of burned up fuels storage on "Lepse".

For adjustment of radiation conditions on "Lepse" in accordance with the present Russian standards in 1990 it was accepted the decision to fill in intertank space of burned up fuels storage on this ship with concrete - conserving agent.

The monolith formed by concrete - conserving agent should become an engineering barrier ensuring increase of strength of all construction and also as immobilization barrier to prevent possible migration of radionuclides from burned up fuels storage in environment.

1.1. Design of intertank space of burned up fuels storage on «Lepse».

The burned up fuels storage on "Lepse" represents located in the nose of the ship rectangular compartment with metallic walls inside of which there are placed two cylindrical tanks with burned up fuel assemblies. Assemblies are placed in capsules arranged by concentric series and intercapsule space is filled by water serving for cooling of capsules. The water circulation is provided with special system. The tanks are closed by rotary covers permitting selectively to open access to capsule and assembly which must be overload.

Burned up assemblies storage has the internal sizes 4800x10150 mm and walls with thickness 420 -450 mm. The tanks having diameter 3600 mm and height 3440 mm are made from stainless steel with thickness 10 mm.

For creation of engineering barrier in intertank space it was necessary to fill it with 102 m³ of cement mixture. It was made with the purpose of strengthening of storage in view of possible accidents at all technological stages of the management of burned up assemblies and at long-term storage in repository.

1.2. General requirements to materials of engineering and immobilization barriers.

To the cured cement mixtures:

- to provide protection of metallic constructions of burned up assemblies storage from corrosion under affect of the external factors; do not accelerate and do not instigate corrosion of available protective contours of storage;
- to be steady against long-lived radiation effect;
- to have high durability, the value of compressive strength of concrete - conserving agent at the end of calculated storage time (500 years) should be not less than 100 kg /cm² (10 MPa);
- to be non-toxic, flame safety and fireproof.

The mixtures prepared for conservation of radiation-hazardous objects must:

- to have flow characteristics indispensable for full filling of space of the complex configuration;
- the used mixtures should be not toxic, are explosion-proof and fireproof;
- mixtures and their rheological characteristics should provide a capability of their mechanical preparation, transport, supply and stacking with usage of equipment serially produced and used in building;
- the materials should be not deficient

1.3. General requirements to technology of conservation of the object:

- the technology of object filling with cement mixtures should be completely mechanized and remotely operated;
- the technological circuit for object cementation should be highly reliable;
- mounting of the part of technological circuit for packing of mixtures in radiation-dangerous zone and process of packing of mixtures should requires of minimum workers participation at carrying out of all requirements and standards of radiation safety.

1.4. Materials and technology for cementation of intertank space.

In accordance with data of radiation safety service of Murmansk marine shipping company the integral radiation dose of concrete in intertank space of burned up assemblies storage for estimated time of storage of "Lepse" will not exceed 1×10^8 rad. Thus for this object it is not required applying of special highly radiation stable concrete. Outgoing from this for filling of intertank space on "Lepse" the concrete on the basis of portland cement and customary fillers (sand, Breakstone) satisfying to GOST 10260-80 was selected. Such concrete mixtures also fit to all, formulated above, requirements: they are not toxic, are fire- and explosion-proof, the materials to their preparation are accessible and mixtures preparation, transport, supply and stacking can be made with usage of serially produced and widely applicable in building equipment.

Due to modern achievements of concrete technology, it is possible to receive not stratified homogeneous mixtures possessing high fluidity, capable to stuff completely internal volumes of objects of the complex configuration.

At the same time, it, as a rule, demands of the heightened consumption of cement. In this connection special attention was paid to limitation of mixture temperature growth during cementation and subsequent curing of concrete monolith to except thermal crackforming in concrete. On the basis of the carried out experimental works for the solution of this problem it was determined to do cementation of intertank space of burned up assemblies storage on "Lepse" in October when climatic conditions near Murmansk allow to receive concrete mixtures with temperature $5-10^{\circ}\text{C}$ without addition cooling. This measure and usage for cooling of curing concrete of cooling system of burned up fuel storage has allowed to limit temperature rise in concrete no more than $35-40^{\circ}\text{C}$ that completely eliminated hazard of dangerous thermal stresses in concrete monolith.

For cementation of intertank space on "Lepse" the concrete mixture on the basis of low aluminate portland cement was used the composition of which is shown in the table 1.1.

Table 3.1.

Composition of concretes used for cementation of intertank space of burned up assemblies storage on "Lepse"

The naming of materials, parameters of concrete mixture	Units of measurement	The consumption of materials on 1 m ³ of concrete	
Portland cement:			
of the mark: "400"	Kg	415	-
"500"	Kg	-	380
Sand	Kg	650	740
Breakstone (size up to 20 mm)	Kg	975	1020
Water : cement ratio		0,48+0,5	0,42+0,45
Additives:			
Superplasticizer		S-3	S-3

Concrete mixtures were prepared on usual concrete plant and transportation of concrete to "Lepse" was made with help of automobile concrete mixers.

The system consisting of the "Wartington" concrete pump and concrete line connected the pump placed on a coast with a receiving hutch on "Lepse" was used for stacking of concrete. In total in intertank space was pumped 110 m³ of concrete, on what it was required about 6 hours.

The check tests have shown that the concrete monolith has no defects, the compression strength of check samples of concrete in the age of 28 day was equal to 27.6 mPa. Thus it is possible to draw a conclusion, that the conservation of burned up assemblies storage on "Lepse" has passed successfully.

2. Decommissioning and preparing to safe storage during 50 years of reactor compartments nuclear submarines in training center of Russian Navy in Paldisk Estonian Republic.

Training center of the USSR Navy in Paldisk was put into exploitation in 1967. There were two real reactor compartments of nuclear submarines and necessary power equipment, (steam generators, turbines etc.). The nuclear power plants in training center were working up to 1989.

After finding by Estonia of the status of the independent state it was raised the question about liquidation of training center of Russian Navy in Paldisk. In accordance with intergovernmental Agreement between Russia and Estonian Republic nuclear objects of training center must be decommissioned and prepared to long-term (50 years) safe storage till 30 September, 1995.

In accordance with this agreement it was carried out complex of works including:

- comprehensive engineering inspection of the objects;
- elaboration and adjustment of the concept of decommissioning and preparation to safe storage of nuclear objects of training center;
- elaboration of the project documentation for carrying out of the works and technology of cementation of reactor compartments and other systems of nuclear power plants;
- hermetic sealing of reactor compartments;
- conservation of reactors, equipment and systems of nuclear power plants;
- building of protective shelters (sarcophagi).

The complex of buildings and facilities of a training center provided realization of all technological operations indispensable for exploitation of reactors and other systems of nuclear power plants in conditions maximum approximated to real.

At exploitation of the installations the carrying out of the following operations was required:

- storage and audit of fresh fuel assemblies, rods of management and protective system etc.;

- recharge of active zones of the reactors;
- replacement of separate components of reactors and equipment of the steam generating installations;
- cooling of the burned up fuel assemblies;
- cooling of radioactive components of reactors and equipment of steam generating installations;
- loading of cooled burned up fuel assemblies on an external transport;
- disposal of the radioactive equipment.

The systems of training center provided carrying out of all these operations.

2.1. Comprehensive engineering inspection of the nuclear objects of the Navy training center.

Comprehensive engineering inspection of nuclear objects of the Navy training center was made to obtain the data necessary for designing of technology and documentation for decommissioning of these objects. The inspection was conducted in two stages. The first stage was done in January, 1994 for elaboration of the concept of decommissioning of nuclear objects and second stage was made after discharge of nuclear fuel from reactors and disposal of liquid and gaseous mediums from systems and equipment to obtain the indispensable additional data for designing technology of objects conservation and preparing of project-budget documentation.

Engineering inspection included:

- estimation of actual condition of buildings, equipment and systems of reactor compartments and other equipment of nuclear power plants;
- itemization of the design and technological solutions on equipment and systems disassembly and their preparing to conservation and long-term storage;
- full-scale measurements of overall dimensions of a reactor compartments necessary for designing of protective shelters;
- radiation examination of reactor compartments, buildings and territory.

On the base of results of engineering inspection the following conclusions were made:

- the dose rate of γ - radiation on territory of training center is equal to 16 -

23 μ R/h and corresponds to background values for the given terrain;

- technical condition of buildings and equipment is satisfactory;
- the radiation examination has shown, that in all placement, excepting reactor compartments, there is no excess of background values β - and γ -activity;
- γ -radiation dose rate in reactor compartments is equal to 0,1 - 23 mR/h.

The obtained results of engineering examination have allowed to accept the optimal and economically reasonable solutions at elaboration of technology and project documentation.

2.2. The concept of decommissioning and preparation to safe storage of nuclear objects of training center

The modern concepts of decommissioning and preparation for long-term storage of nuclear objects envisage their deep decontamination and disassembly, including constructions with induced radiation. The realization of the similar concepts is connected with formation big quantity of highly active solid radioactive wastes and secondary liquid radioactive wastes. Processing and solidification of these wastes are very complex, expensive and long-timed processes requiring of creation of new productions.

In conditions of a nuclear training center in Paldisk the indicated concept could not be used because of very short period of time which was given on all works (nuclear objects of training center must be delivered to Estonian party till September, 1995) and also because of the limited financial capabilities of Russian party. All this dictated necessity of acceptance of new more optimal solutions.

In view of IAEA principles of safety and technical criterions for underground disposal of the radioactive wastes (serial of issues on safety, No 99, Vienna 1990, the section 3 "Principles of safety") was necessary to find a solution answering to the following requirements:

- providing of safety ;
- liability before the future generations;
- consequences in the future: " It is necessary to ensure a degree of isolation of highly radioactive wastes at such level that there were absent predictable kinds of risk for people health or consequence for ar

environment in the future, which would not be acceptable today".

For carrying out of the indicated conditions and requirements, on fifty years period of reactor compartments storage in accordance with really existing radiation situation, it was necessary to create a number of engineering barriers precluding migration of radionuclides in environment and eliminating unauthorized admittance of the people into reactor compartments.

The following system of reactor compartments preparation to long-term storage was adopted to realization:

- preparing of devices and systems of reactor compartments and steam generating installation to conservation with the help of concrete - conserving agents;
- creation immobilizing and engineering barriers inside reactor compartments;
- building protective sarcophagi outside of reactor compartments designed for protection of reactor compartments from extreme impacts natural and technical origin within 50 years.

The preparation of devices and submarine inner compartments and of steam generating installation to constitutes barriers for disassembly and deleting of the uncontaminated equipment was done prior to sealing reactor compartments. The hermetic sealing involved plugging pipe lines, holes in body of reactor compartments with grout prior to the compartment test on air-tightness. Besides these works dehumidifying of air inside reactor compartments and deposition of outside protective coatings on bodies of compartments were made.

In result of engineering inspection the list of equipment and devices of reactor compartments must be conserved with help of special concrete mixtures was determined.

On the basis of results of researches of properties of special portland cement mixtures, presented in this review, for conservation of reactor compartments the mixture No 2 was selected, in which as the main components of mixture except of cement will be used finely divided shungizit and shungizit sand. For giving high fluidity to concrete mixture in it the superplasticizer S-3 was added, and for increase of concrete gas permeability the component SDO was introduced.

The composition of concrete, which were used for conservation of reactor compartments and the creation of external shelters (sarcophagi) are shown below.

Composition of concrete mixture No 2 for conservation of reactor compartments (consumption of materials on 1 m³ of concrete):

Portland cement of Pikalev plant M 500	- 726 kg
Shungizit filling material	- 259 kg
Shungizit sand	- 621 kg
Water	- 372 kg
Superplasticizer S-3	- 5.4 kg
SDO	- 0.4 kg

Mean density of concrete of 2000 kg / m³

For building external shelters the concrete of the following composition was used (consumption of materials on 1 m³ of concrete):

Portland cement of Pikalev plant of M 400	- 400 kg
Sand	- 512 kg
Breakstone (fraction no more than 10 mm)	- 836 kg
Water	- 246 kg
Superplasticizer S-3	- 6.0 kg

Mean density of concrete of 2000 kg / m³.

All activities on conservation of the equipment of reactor compartments and building of external shelters were finished to the end of September, 1995 and were adopted by the Estonian party which stated that the carried out works guaranteed safety of decommissioned reactor compartments on demanded period (50 years).

CONCLUSION.

The results of done researches have shown that the composition of portland cement mixtures has high influence on properties of these mixtures. Changing composition of cement mixtures it is possible to obtain mixtures possessing complex of properties in the most degree adequate to areas of their applying.

In the present review we considered two fields of application of portland cement mixtures:

- conservation (closure) of radiation - hazardous objects of atomic engineering, in particular of waste tanks, reactor compartments of vessels with nuclear energy installations etc.;
- solidification and preparing for long-term storage of the liquid radwastes.

The optimal complex of properties of cement mixtures designed for applying in each of introduced above areas can be various.

So at usage of these mixtures for conservation of radiation - hazardous objects with high-level of radiation the important value has a high gas permeability of using mixtures because that allows to ensure going out of radiolytical gases without disturbance of concrete monolith integrity. For cement mixtures intended for solidification of the liquid radwastes middle and low level of activity the requirements of low leaching rate of radionuclides and high stability of mixture at affect of groundwater and other factors of environment of radwastes storage are going on the foreground.

Considering from these positions results of researches of portland cement mixtures it is possible to make following conclusions.

For conservation (closure) of radiation-hazardous objects with high level of radiation for which the release of significant amount of radiolytical hydrogen is possible, the most favourable combination of properties has the composition No 2, as it has a high gas permeability that provides output of hydrogen from massive of the cured composition without disturbance of it integrity.

For conservation of radiation-hazardous objects with low radiation level, for which quantity of emanation of radiolytical hydrogen is insignificant, and for solidification of the liquid radwastes the preference is necessary to give to composition No 21, which has a low permeability, low rate of radionuclides leaching and highest stability to affect of groundwater from studied compositions on the basis of portland cement. Estimation of possible service time of composition No 21 showed that even in disadvantageous condition (groundwater flow in repository up to 100 m/year) durability of it must be more 500 years – the time which is necessary for practically full decay of Cs-137 and Sr-90.

The technologies of cementation of radiation-hazardous objects of nuclear fleet was elaborated with accounting of results of carried out investigation. This permitted to make up to date the large scale works on conservation with help of concrete of two objects of nuclear fleet:

- floating technical base "Lepse" (ship assigned to maintenance of atomic ice breakers) of Murmansk marine shipping company;
- two reactor compartments of nuclear submarines in former training center of the Russian Navy in Paldisk, Estonia.

In the short review it is impossible to present all results obtained in cement mixtures researches carried out in Russia. But presented results permits to formulate key technical questions that can be the matter of analytical and experimental investigations in the potential Part 2 of the project:

- elaboration of new compositions of mixtures on the base of cement and other inorganic binders for liquid radwastes solidification and for closure of tanks and other radiation-hazardous objects;
- looking for additives to cement which can strongly retain in cement matrixes the certain radionuclides (Cs-137, Sr-90, Tc-99, I-129, Np-237);
- investigation of radiation-chemical processes taking place at cement mixtures irradiation to look up of the ways of decreasing of hydrogen generation.

REFERENCES.

1. F. P. Glasser. Cement and Concrete Research, v 22, N 2/3, pp. 201-216 (1992) .
2. P. G. Komokhov et al. Rep. PGUPS N 2074 (1994).
3. R. A. Bulman, J. P. Cooper. Speciation of Fission and Activated Products in the Environment. Proc. of Speciation-85 Seminar, pp. 157-161. Elsv. Applied Sci. London (1986).
4. R. J. Day, F. P. Glasser. Fly Ash and Coal Conversion By-Products. Characterisation, Utilisation and Disposal IV. Materials Res. Symp. Proc. Pittsburg P. A. V 176 (1990).
5. V. M. Malhotra. Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete. Am. Concr. Inst. Detroit Special Publ. 91 (1986).
6. V. M. Malhotra. Superplasticizers and Other Chemical Admixtures in Concrete. Am. Concr. Inst. Detroit Special Publ. 119 (1989).
7. T. Izumoda et al. Nuclear Technol. 7, 185-190 (1987).
8. V. M. Oversby, P. W. Rrown. Scientific Basis for Nuclear Waste Manag. Mat. Res. Soc. Pittsburg P.A. v 176, pp. 15-20 (1990).
9. W. E. Clark, C. I. Thompson. US Patent 4017417A (1977).
10. M. Atkins et al. Waste Management, 10, 303-308 (1990).
11. M. J. Plodinec. Rep. DP-1444, Sav. Riv. Plant (1976).
12. F. P. Glasser et al. Immobilization and Leaching Mechanisms of Radwaste in Cement Based Mixtures. Rep. DOE-RW-2-108 (1982).
13. R. M. Nielson. Trans. Am. Nucl. Soc. 265, 290 (1977).
14. H. Christensen, E. Bjerbakke. Radiolysis of Concrete. SICBF-KBS TR-84-02 (Stocholm) (1984).
15. C. R. Wilding et al. Commission of European Communities. Rep. Eur 13559 (1981).
16. C. R. Wilding. Cement and Concrete Research v 22, pp. 293-310 (1992).
17. A. K. Pikaev. Dozimetriya v radiacionnoy khimii. M. Nauka. 1975.
18. E. D. Heske. Ispytanie otverjdenykh radioaktivnykh otkhodov na vychelachivanie. AINF N 155(11), M, 1971.
19. Opreделение khimicheskoy stoykosti tsementirovannykh RAO. GOST 29114-91.

20. A. K. Pikaev. Sovremennaya radiatsionnaya khimiya. Nauka. Moskva. 1986.
21. Otbor prob i analiz prirodnkh gazov nefte -gazovykh basseynov. Red. I.S. Sterobinetch, M. K. Kalinko. M, Nedra, 1994.
22. I. L. Gufeld et al. DAN v 328, N 1 < pp 39-42 (1993).
23. Bepo G. et al. Euroatom Information 6, 650 (1968).
24. Brigeovich R. F. , Kuznetsov P.A. Radiokhimiya, v 9, 693 (1967).
25. The Radiochemistry of Fluorine, Chlorine, Bromine.
26. J. Cranc. Mathematics of Diffusion. 2 -nd Ed. Claridon Press, Oxford, 1975.
27. S. L. Golyenko-Volfson et al. Khimichiskie osnovy tekhnologii i primeneniya fosfatnykh svyazok i pokrytiy. Khimiya, 1968.
28. E. I. Kazantsev et al, Ionoobmennyye materialy, ikh sintez i svoystva. UGI, Ekaterinburg, 1969.
29. L. P. Prokhorov et al. Patent USSR N 176127, MKI G21f9/16
30. G. B. Borisov et al. Rep. MCC and VNIINM N 31006, 1984.

5.0 ATTACHMENT B

Russian Low-Level Radioactive Waste Regulations (in Russian) **January 1, 2002**

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ФЕДЕРАЛЬНЫЙ НАДЗОР РОССИИ
ПО ЯДЕРНОЙ И РАДИАЦИОННОЙ БЕЗОПАСНОСТИ
(ГОСАТОМНАДЗОР РОССИИ)

ПОСТАНОВЛЕНИЕ

27 сентября 2000 г.

МОСКВА

№ 2

Об утверждении и введении в действие федеральных норм и правил в области использования атомной энергии НП-019-2000 "Сбор, переработка, хранение и кондиционирование жидких радиоактивных отходов. Требования безопасности"

Федеральный надзор России по ядерной и радиационной безопасности

ПОСТАНОВЛЯЕТ:

Утвердить и ввести в действие с 1 января 2001 г. федеральные нормы и правила в области использования атомной энергии НП-019-2000 "Сбор, переработка, хранение и кондиционирование жидких радиоактивных отходов. Требования безопасности".

Начальник
Госатомнадзора России

Ю.Г. Вишневецкий
Ю.Г. Вишневецкий

Новоселов С.И.

по поручению Г.И. Новикова в соответствии с поручением Г.И. Новикова

Госатомнадзора России

по поручению Г.И. Новикова в соответствии с поручением Г.И. Новикова

24.10.2000
2025/6-1

Федеральный надзор России по ядерной и радиационной безопасности
(Госатомнадзор России)

ФЕДЕРАЛЬНЫЕ НОРМЫ И ПРАВИЛА
В ОБЛАСТИ ИСПОЛЬЗОВАНИЯ АТОМНОЙ ЭНЕРГИИ

УТВЕРЖДЕНЫ
постановлением
Госатомнадзора России
от 27 сентября 2000 г.
№ 7

СБОР, ПЕРЕРАБОТКА, ХРАНЕНИЕ И КОНДИЦИОНИРОВАНИЕ
ЖИДКИХ РАДИОАКТИВНЫХ ОТХОДОВ.
ТРЕБОВАНИЯ БЕЗОПАСНОСТИ

НП - 019 - 2000

ВВЕДЕНА в действие
с 1 января 2001 г.

Москва 2000

УДК 621.039.58

**СБОР, ПЕРЕРАБОТКА, ХРАНЕНИЕ И КОНДИЦИОНИРОВАНИЕ ЖИДКИХ
РАДИОАКТИВНЫХ ОТХОДОВ. ТРЕБОВАНИЯ БЕЗОПАСНОСТИ**

**Госатомнадзор России
Москва, 2000**

Настоящие федеральные нормы и правила "Сбор, переработка, хранение и кондиционирование жидких радиоактивных отходов. Требования безопасности" устанавливают требования к обеспечению безопасности при сборе, переработке, хранении и кондиционировании жидких радиоактивных отходов на ядерных установках, радиационных источниках, в пунктах хранения ядерных материалов и радиоактивных веществ, хранилищах РАО.

Нормативный документ выпускается впервые.

Нормативный документ разработан в Научно-техническом центре по ядерной и радиационной безопасности при участии Захаровой К.П., Масанова С.Л. (ВНИИНМ им. А.А. Бочвара) Киселева В.В. (ФУМБ и ЭП при Минздраве России), Непейвко М.А., Шарафутдинова Р.Б. (НТЦ ЯРБ).

При разработке нормативного документа рассмотрены и учтены замечания: ФУМБ и ЭП при Минздраве России, Госкомэкологии России, УЗ и СЭЯО Минатома России, ДБЗ и ЧС Минатома России, ВНИИНМ им. А.А. Бочвара, МосНПО "Радон", ВНИПИЭТ, ГНЦ "Институт биофизики", Горно-химического комбината, Сибирского химического комбината, ПО "Маяк", концерна "Росэнергоатом", Ленинградской АЭС и др.

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нормами и правилами в области использования атомной энергии. Отнесение указанных веществ, материалов, изделий, приборов, оборудования и объектов к радиоактивным отходам определяется эксплуатирующей организацией и обосновывается в проекте ядерной установки, радиационного источника и пункта хранения.

17. Переработка ЖРО - технологические операции по сокращению объема, изменению агрегатного состояния и (или) физико-химических свойств ЖРО.

18. Программа обеспечения качества - документально оформленный комплекс организационно-технических и других мероприятий по обеспечению качества, позволяющих руководству эксплуатирующей организации и (или) организаций, выполняющих работы и предоставляющих услуги эксплуатирующей организации, убедиться в том, что вся деятельность, влияющая на ядерную и радиационную безопасность, осуществляется в соответствии с требованиями федеральных норм и правил в области использования атомной энергии и других нормативных документов.

19. Сбор ЖРО - сосредоточение ЖРО в специально оборудованных емкостях.

20. Упаковка РАО - упаковочный комплект (контейнер) с помещенными в него РАО, подготовленный для транспортирования, и (или) хранения, и (или) захоронения.

21. Цементирование ЖРО - включение ЖРО в цементный матричный материал.

22. Хранение ЖРО - временное содержание ЖРО в емкостях (хранилищах), обеспечивающих защиту от радиации и изоляцию ЖРО, с намерением последующего извлечения ЖРО.

2. НАЗНАЧЕНИЕ И ОБЛАСТЬ ПРИМЕНЕНИЯ

2.1. Настоящий документ устанавливает требования к обеспечению безопасности при сборе, переработке, хранении и кондиционировании ЖРО на ядерных установках, радиационных источниках, в пунктах хранения ядерных материалов и радиоактивных веществ, хранилищах РАО (далее - пункты хранения).

2.2. Настоящий документ распространяется на проектируемые, сооружаемые, эксплуатируемые и выводимые из эксплуатации ядерные установки, радиационные источники и пункты хранения при сборе, переработке, хранении и кондиционировании ЖРО.

2.3. Настоящий документ не распространяется на:

- обращение с ЖРО, образующимися при добыче и обогащении руд радиоактивных веществ и других полезных ископаемых;
- обращение с ЖРО, накопленными в поверхностных водоемах объектов ядерного топливного цикла.

3. ОБЩИЕ ТРЕБОВАНИЯ К ОБЕСПЕЧЕНИЮ БЕЗОПАСНОСТИ ПРИ СБОРЕ, ПЕРЕРАБОТКЕ, КОНДИЦИОНИРОВАНИИ И ХРАНЕНИИ ЖИДКИХ РАДИОАКТИВНЫХ ОТХОДОВ

3.1. Технические средства и организационные меры по обеспечению радиационной безопасности при сборе, переработке, хранении и

кондиционировании ЖРО на ядерной установке, радиационном источнике и в пункте хранения должны определяться исходя из максимальной допустимой активности ЖРО на этих объектах и ограничивать радиационное воздействие на работников (персонал), население и окружающую среду уровнями, установленными Нормами радиационной безопасности (НРБ-99) и другими федеральными нормами и правилами в области использования атомной энергии и нормативными документами.

3.2. В проекте ядерной установки, радиационного источника и хранения должны быть предусмотрены конкретные технические средства безопасного сбора, переработки, хранения и кондиционирования разработанные в соответствии с требованиями настоящего документа, других федеральных норм и правил в области использования атомной энергии, и нормативных документов.

При отсутствии необходимых нормативных документов предлагаемые конкретные технические решения устанавливаются и обосновываются в проекте ядерной установки, радиационного источника и пункта хранения в соответствии с достигнутым уровнем науки и техники.

3.3. Требования к конструированию, изготовлению и монтажу оборудования, предназначенного для сбора, переработки, хранения и кондиционирования ЖРО, проектированию соответствующих систем (элементов) ядерных установок, радиационных источников и пунктов хранения, а также классификация систем (элементов) и оборудования ЖРО, предназначенных для сбора, переработки, хранения и кондиционирования ЖРО, по назначению, влиянию на безопасность и по характеру выполняемых ими функций безопасности, категориям сейсмостойкости, пожаро- и взрывоопасности устанавливаются федеральными нормами и правилами в области использования атомной энергии, регламентирующими обеспечение безопасности ядерных установок, радиационных источников и пунктов хранения и настоящим документом.

3.4. Устройство и надежность систем (элементов) ядерной установки, радиационного источника и пункта хранения, документация и работы по сбору, переработке, хранению и кондиционированию ЖРО должны являться объектами деятельности эксплуатирующих организаций и (или) организаций, выполняющих работы и предоставляющих услуги эксплуатирующим организациям, по обеспечению качества в соответствии с программой обеспечения качества эксплуатирующей организации, требованиями федеральных норм и правил в области использования атомной энергии и других нормативных документов.

3.4.1. Программа обеспечения качества должна быть изложена на:

- организацию эффективной системы подготовки, переподготовки, повышения квалификации и аттестации работников (персонала);
- минимизацию образующихся ЖРО по величине их активности, массе и объему;
- контроль качества поставляемого оборудования, комплектующих изделий и материалов;
- получение достоверной и полной информации о количественном и качественном составе ЖРО в местах их образования, сбора, переработки, хранения и кондиционирования;

организацию контроля качества проведения технологических процессов при сборе, переработке, хранении и кондиционировании ЖРО;

- установление системы критериев качества ЖРО, которым ЖРО должны отвечать после сбора, переработки, хранения и кондиционирования;
- использование метрологически аттестованных методик контроля качества ЖРО и испытаний упаковок кондиционированных отходов;
- организацию контроля качества ЖРО и упаковок кондиционированных отходов;
- организацию эффективной системы записей и хранения документации при сборе, переработке, хранении и кондиционировании ЖРО, включая идентификационную маркировку упаковок кондиционированных отходов.

3.4.2. В зависимости от стадии обращения с ЖРО при установлении критериев качества ЖРО должны учитываться основные характеристики ЖРО, контейнера и упаковки ЖРО.

3.4.2.1. Характеристики ЖРО:

- химический состав и фазовое состояние;
- величина суммарной активности;
- радионуклидный состав, величина удельной альфа- и бета-активности.

3.4.2.2. Характеристики отвержденных ЖРО:

3.4.2.2.1. Битумный компаунд:

- радионуклидный состав, величина удельной альфа- и бета-активности, мощность эквивалентной дозы;
 - содержание свободной воды в компаунде;
 - водоустойчивость;
 - термическая устойчивость;
 - радиационная устойчивость;
 - биологическая устойчивость.

3.4.2.2.2. Цементный компаунд:

- радионуклидный состав, величина удельной альфа- и бета-активности, мощность эквивалентной дозы;
 - водоустойчивость;
 - механическая прочность;
 - радиационная устойчивость;
 - термическая устойчивость.

3.4.2.2.3. Стеклоподобные материалы:

- радионуклидный состав, величина удельной альфа- и бета-активности, мощность эквивалентной дозы;
 - состав фосфатных материалов;
 - однородность отвержденного материала;
 - тепловыделение;
 - водоустойчивость;
 - термическая стойкость;
 - радиационная стойкость;
 - механическая прочность;
 - теплофизические константы (теплопроводность, коэффициент термического расширения).

3.4.2.4. Характеристики контейнера ЖРО:

- коррозионная стойкость, радиационная стойкость, конфигурация (геометрические размеры) - для металлического контейнера;
- плотность, пористость, водопроницаемость, газопроницаемость, морозостойкость, радиационная стойкость, стойкость микроорганизмам, плесени и грибкам, пожаростойкость, конфигурация (геометрические размеры) - для железобетонного контейнера;
- иные характеристики, определяющие изолирующую способность контейнера.

3.4.2.5. Характеристики упаковки ЖРО:

- радионуклидный состав, величина удельной альфа- и бета-активности, мощность эквивалентной дозы;
- величина суммарной активности;
- однородность;
- механическая прочность (статические, динамические, ударные нагрузки);
- устойчивость к тепловым нагрузкам и термическим циклам;
- радиационная устойчивость.

3.4.3. Система контроля качества ЖРО и кондиционированных отходов:

должна включать контроль качества:

- процесса сбора ЖРО;
- ЖРО, направляемых на переработку;
- процесса переработки ЖРО;
- матричных материалов;
- процесса отверждения ЖРО;
- отвержденных ЖРО;
- упаковок кондиционированных отходов.

Объем контроля качества устанавливается в проекте ядерной установки, радиационного источника и пункта хранения и должен обеспечивать получение достоверной информации о характеристиках ЖРО, матричных материалов, отвержденных ЖРО и упаковках кондиционированных отходов.

3.4.4. В программе обеспечения качества должны быть установлены порядок и процедуры регистрации нарушений критериев качества ЖРО, кондиционированных отходов, а также организации сбора, обработки и анализа данных о нарушениях и причинах их возникновения.

По результатам анализа причин нарушений должны разрабатываться и приниматься корректирующие меры по предотвращению их повторения.

3.4.5. -Эксплуатирующая организация должна контролировать эффективность реализации программы обеспечения качества на ядерной установке, радиационном источнике и в пункте хранения путем проведения проверок (инспекций), включающих:

- верификацию ведения технологических процессов при сборе, переработке, кондиционировании и хранении ЖРО в рамках установленных проектом параметров в соответствии с требованиями федеральных норм и правил в области использования атомной энергии и условиями действия лицензии государственного органа регулирования безопасности при использовании атомной энергии;
- проверку работоспособности систем управления технологическими процессами и их контроля;

- проверку соответствия качества ЖРО и упаковок кондиционированных отходов критериям качества.

По всем выявляемым при проверках (инспекциях) случаям соответствия должны быть приняты корректирующие меры.

3.5. При сборе, переработке, хранении и кондиционировании ЖРО должно обеспечиваться:

- поддержание требуемого уровня безопасности при обращении с ЖРО как с источниками ионизирующего излучения;
- исключение необоснованного облучения работников (персонала);
- сведение к разумно достижимому низкому уровню облучения работников (персонала) и населения с учетом санитарных правил, норм и гигиенических нормативов, экономических и социальных факторов;
- предотвращение возможных аварий с радиационными последствиями и ослабление их последствий в случае их возникновения;
- сокращение объема ЖРО;
- подготовка ЖРО к хранению и (или) захоронению после их кондиционирования.

3.6. Проектом ядерной установки, радиационного источника и пункта хранения должна быть установлена классификация помещений, предназначенных для сбора, переработки, хранения и кондиционирования ЖРО, по взрыво- и пожарной безопасности в соответствии с требованиями федеральных норм и правил в области использования атомной энергии.

Конкретные технические решения и организационные меры по обеспечению взрывозащиты и противопожарной защиты при сборе, переработке, хранении и кондиционировании ЖРО устанавливаются и обосновываются в проекте ядерной установки, радиационного источника и пункта хранения.

3.7. Помещения, предназначенные для сбора, переработки, хранения и кондиционирования ЖРО, должны быть оборудованы системой вентиляции, предотвращающей загрязнение воздушной среды помещений и окружающей среды радиоактивными веществами и поддерживающей климатические условия, необходимые для нормальной эксплуатации оборудования. Загрязненный из помещений загрязненный воздух и из оборудования газы перед сбросом в атмосферу должны подвергаться очистке.

3.8. При сборе, переработке, хранении и кондиционировании ЖРО должны быть предусмотрены:

- технические средства и организационные меры по обеспечению физической защиты ЖРО;
- технические средства и организационные меры по предотвращению протечек ЖРО и иных процессов, приводящих к поступлению радионуклидов в окружающую среду в количестве, превышающем пределы, установленные санитарными правилами, нормами и гигиеническими нормативами, федеральными нормами и правилами в области использования атомной энергии;
- радиационный контроль, включающий: контроль загрязненности поверхностей помещений, оборудования и трубопроводов, мощности эквивалентной дозы, удельной активности и радионуклидного состава ЖРО.

Средства и объем радиационного контроля устанавливаются в прсекте ядерной установки, радиационного источника и пункта хранения в соответствии с требованиями санитарных правил, норм и гигиенических нормативов, федеральных норм и правил в области использования атомной энергии.

3.9. При сборе, переработке, хранении и кондиционировании ЖРО должна быть исключена возможность:

- неконтролируемого изменения агрегатного состояния ЖРО, в том числе образование осадков и отложений;
- неконтролируемого возникновения экзотермических реакций;
- неконтролируемого образования коррозионно агрессивных веществ.

3.10. При сборе, переработке, хранении и кондиционировании ЖРО, содержащих ядерно-опасные делящиеся материалы, должна быть исключена возможность возникновения СЦР.

Конструкция и геометрические размеры оборудования, предназначенного для сбора, переработки, хранения и кондиционирования ЖРО, содержащих ядерно-опасные делящиеся материалы, а также порядок проведения работ не должны приводить к возникновению СЦР.

Содержание ядерно-опасных делящихся материалов в кондиционированных ЖРО и геометрическая форма их упаковок должны исключать возможность возникновения СЦР.

Помещения, в которых находится оборудование, предназначенное для сбора, переработки, хранения и кондиционирования ЖРО, содержащих ядерно-опасные делящиеся материалы, должны быть оснащены системой аварийной сигнализации САС, которая должна эксплуатироваться в режиме постоянной готовности обнаружения СЦР.

Обеспечение ядерной безопасности при сборе, переработке, хранении и кондиционировании ЖРО, содержащих ядерно-опасные делящиеся материалы, регламентируется федеральными нормами и правилами в области использования атомной энергии, определяющими правила ядерной безопасности.

3.11. При сборе, переработке, хранении и кондиционировании ЖРО должна быть предусмотрена возможность дезактивации оборудования, трубопроводов, контейнеров и помещений. Оборудование, трубопроводы и поверхности помещений, предназначенные для сбора, переработки, хранения и кондиционирования ЖРО, должны обладать коррозионной стойкостью в агрессивных средах, низкой сорбирующей способностью по отношению к радиоактивным веществам и легко дезактивироваться.

3.12. Сбор, переработка, хранение и кондиционирование ЖРО совместно с нерадиоактивными отходами не разрешается.

3.13. Сбор, переработка, хранение и кондиционирование ЖРО должны документироваться в соответствии с программой обеспечения качества. Каждая партия (упаковка) ЖРО на всех этапах обращения должна сопровождаться документацией, содержащей ее основные характеристики, в том числе:

3.13.1. Сбор ЖРО:

- источник образования;
- количество;
- химический состав и фазовое состояние;
- величина суммарной активности;

ПЕРЕЧЕНЬ СОКРАЩЕНИЙ

ЖРО - жидкие радиоактивные отходы

РАО - радиоактивные отходы

САС - система аварийной сигнализации

СЦР - самоподдерживающаяся цепная реакция деления

ХЖО - хранилище жидких радиоактивных отходов

1. ОСНОВНЫЕ ТЕРМИНЫ И ОПРЕДЕЛЕНИЯ

1. Битумирование ЖРО - включение РАО в битумный матричный материал.
 2. Водоустойчивость - способность компаунда (упаковки) сохранять свои свойства и удерживать включенные в него радионуклиды при контакте с водой.
 3. Выдержка ЖРО - хранение ЖРО с целью снижения радиоактивности и тепловыделения за счет распада короткоживущих радионуклидов.
 4. Достигнутый уровень науки и техники - комплекс научных и технических знаний, техно-логических, проектных и конструкторских разработок в определенной области науки и техники, который подтвержден научными исследованиями и практическим опытом и отражен в научно-технических материалах.
 5. Компаунд - матричный материал с включенным в него РАО.
 6. Кондиционирование ЖРО - операции по изготовлению упаковки, пригодных для безопасного хранения и (или) транспортирования и (или) захоронения. Кондиционирование может включать перевод ЖРО в стабильную форму, помещение ЖРО в контейнеры.
 7. Контейнер для РАО - емкость, используемая для сбора, и (или) транспортирования, и (или) хранения, и (или) захоронения РАО.
 8. Корректирующие меры - деятельность, с помощью которой устраняются несоответствия и предотвращается их повторение.
 9. Материал матричный - нерадиоактивный материал, используемый для иммобилизации ЖРО в монолитную структуру.
- П р и м е ч а н и е. Примерами матричных материалов являются битум, цемент, стеклоподобные материалы.
10. Обращение с ЖРО - все виды деятельности, связанные со сбором, транспортированием, переработкой, кондиционированием, хранением и (или) захоронением ЖРО.
 11. Обеспечение качества при обращении с РАО - планируемая и систематически осуществляемая деятельность, направленная на то, чтобы все работы по обращению с РАО, влияющие на ядерную и радиационную безопасность, проводились в соответствии с требованиями федеральных норм и правил в области использования атомной энергии и других нормативных документов, а их результаты удовлетворяли предъявленным требованиям.
 12. Остекловывание ЖРО - перевод РАО в стеклоподобное состояние.
 13. Отверждение ЖРО - перевод ЖРО в твердое агрегатное состояние с целью уменьшения возможности миграции радионуклидов в окружающую среду.
 14. Отходы жидкие радиоактивные - РАО в виде жидких продуктов (водных или органических) или пульп, содержащих радионуклиды в растворенной форме или в виде взвесей.
 15. Отходы жидкие радиоактивные органические - ЖРО в виде масел, эмульсий масел в воде, растворов детергентов, экстрагентов и т.п.
 16. Отходы радиоактивные - не подлежащие дальнейшему использованию вещества в любом агрегатном состоянии, материалы, изделия, приборы, оборудование, объекты биологического происхождения, в которых содержание радионуклидов превышает уровни, установленные федеральными

- радионуклидный состав, величина удельной альфа- и бета-активности, дата их определения;
- тип контейнера (для упаковки ЖРО);
- дата упаковки (для упаковки ЖРО);
- мощность эквивалентной дозы (для упаковки ЖРО);
- поверхностное загрязнение контейнера (для упаковки ЖРО);
- идентификационный знак упаковки (для упаковки ЖРО);
- место хранения;
- соответствие критериям качества.

3.13.2. Переработка ЖРО:

- источник образования;
- методы переработки;
- количество;
- химический состав и фазовое состояние;
- величина суммарной активности;
- радионуклидный состав, величина удельной альфа- и бета-активности, дата их определения;
- тип контейнера (для упаковки ЖРО);
- дата упаковки (для упаковки ЖРО);
- мощность эквивалентной дозы (для упаковки ЖРО);
- поверхностное загрязнение контейнера (для упаковки ЖРО);
- идентификационный знак упаковки (для упаковки ЖРО);
- место хранения.

3.13.3. Отверждение ЖРО:

- источник образования;
- методы переработки;
- количество;
- величина суммарной активности;
- радионуклидный состав, величина удельной альфа- и бета-активности, дата их определения;
- тип контейнера;
- дата упаковки;
- мощность эквивалентной дозы от упаковки ЖРО;
- поверхностное загрязнение контейнера;
- идентификационный знак упаковки;
- место хранения.

3.13.4. Кондиционирование ЖРО:

- источник образования;
- количество;
- методы переработки;
- метод кондиционирования;
- величина суммарной активности;
- радионуклидный состав, величина удельной альфа- и бета-активности, дата их определения;
- тип и размер контейнера;
- дата упаковки;
- поверхностное загрязнение контейнера, мощность эквивалентной дозы от упаковки и дата их определения;
- идентификационный знак упаковки;
- место хранения.

4. ТРЕБОВАНИЯ К ОБЕСПЕЧЕНИЮ БЕЗОПАСНОСТИ ПРИ СБОРЕ ЖИДКИХ РАДИОАКТИВНЫХ ОТХОДОВ

4.1. Сбор ЖРО должен являться обязательным этапом подготовки их к переработке, хранению и кондиционированию и обеспечивать исключение поступления радионуклидов в окружающую среду выше пределов, установленных санитарными правилами, нормами и гигиеническими нормативами, федеральными нормами и правилами в области использования атомной энергии, путем сосредоточения ЖРО в специальном оборудовании.

4.2. Сбор ЖРО должен проводиться отдельно в зависимости от:

- периода полураспада радионуклидов (менее 15 суток, более 15 суток);
- величины удельной активности;
- концентрации альфа-активных радионуклидов;
- химического состава;
- фазового состояния;
- предполагаемого способа переработки.

4.3. Органические взрыво- и пожароопасные ЖРО должны собираться отдельно от других видов ЖРО.

4.4. При сборе неорганических ЖРО должны собираться отдельно:

- малосолевые водные растворы (с концентрацией солей менее 1 г/л);
- высокосолевые водные растворы (с концентрацией солей более 1 г/л);
- щелочные металлы, использованные в качестве теплоносителя;
- сильные окислители;
- коррозионно-активные вещества;
- химически неустойчивые вещества;
- ионообменные смолы;
- перлит, вермикулит и др.;
- титановые сорбенты;
- шламы.

4.5. Сбор ЖРО должен производиться с одновременным учетом требований пп. 4.1–4.4 в последовательности, обеспечивающей минимально возможное облучение работников (персонала). Последовательность операций по сбору ЖРО устанавливается и обосновывается в проекте ядерной установки, радиационного источника и пункта хранения.

4.6. Сборники (емкости, контейнеры и т.д.) ЖРО должны располагаться как можно ближе к месту образования отходов.

4.7. ЖРО, содержащие только радионуклиды с периодом полураспада менее 15 суток, должны собираться отдельно и подлежат выдержке в местах временного хранения ЖРО до снижения величины их удельной активности и величины их суммарной активности до значений, при которых радиоактивные вещества освобождаются от регламентации Нормами радиационной безопасности (НРБ-99).

4.8. Для сбора ЖРО должна быть предусмотрена система специальной канализации (спецканализация). Если количество образующихся ЖРО не превышает 200 л/сут. для их сбора могут использоваться контейнеры (сборники). Требования к контейнерам (сборникам) устанавливаются нормативными документами.

4.9. Сброс ЖРО в хозяйственно-фекальную канализацию, производственно-ливневую канализацию, в поверхностные водоемы, поглощающие ямы, колодцы, скважины, на поля орошения, поля фильтрации и на поверхность земли запрещается.

5. ТРЕБОВАНИЯ К ОБЕСПЕЧЕНИЮ БЕЗОПАСНОСТИ ПРИ ПЕРЕРАБОТКЕ ЖИДКИХ РАДИОАКТИВНЫХ ОТХОДОВ

5.1. Переработка ЖРО должна обеспечивать очистку жидкой фазы ЖРО и концентрирование радионуклидов в меньшем объеме.

Не допускается полное обезвоживание высокосолевых водных растворов ЖРО в случае возможного экзотермического взаимодействия компонентов сухого остатка ЖРО.

Конкретные технические методы и средства переработки ЖРО устанавливаются и обосновываются в проекте ядерной установки, радиационного источника и пункта хранения.

5.2. При передаче (транспортировании) солевых концентратов (кубовых остатков) ЖРО к месту их хранения и отверждения должны быть приняты меры по предотвращению образования отложений в трубопроводах и оборудовании.

5.3. Образующиеся в результате переработки ЖРО солевые концентраты, отработавшие сорбенты, шламы, осадки должны быть кондиционированы в соответствии с требованиями настоящего документа.

5.4. Если концентрация радионуклидов и вредных веществ в образующихся в результате переработки ЖРО очищенных водах не превышает допустимых концентраций, установленных в соответствии с требованиями санитарных правил, норм и гигиенических нормативов, федеральных норм и правил в области использования атомной энергии, то они могут быть использованы для собственных нужд в системе оборотного водоснабжения ядерной установки, радиационного источника и пункта хранения или сбрасываться в открытую гидросеть через промежуточную контрольную емкость.

6. ТРЕБОВАНИЯ К ОБЕСПЕЧЕНИЮ БЕЗОПАСНОСТИ ПРИ ХРАНЕНИИ ЖИДКИХ РАДИОАКТИВНЫХ ОТХОДОВ

6.1. При хранении ЖРО должно обеспечиваться исключение:

- неоправданного облучения работников (персонала);
- облучения населения выше установленных пределов;
- поступления радионуклидов в окружающую среду выше пределов, установленных федеральными нормами и правилами в области использования атомной энергии и другими нормативными документами.

6.2. В проекте ядерной установки, радиационного источника и пункта хранения должны быть предусмотрены технические средства и организационные меры по безопасному хранению ЖРО, а также установлены и обоснованы допустимые объемы ЖРО, их радионуклидный состав, величина активности и сроки хранения ЖРО.

6.3. Хранение больших объемов ЖРО должно осуществляться в специально оборудованных хранилищах с системой барьеров, предотвращающей поступление радионуклидов в окружающую среду выше

пределов, установленных федеральными нормами и правилами в области использования атомной энергии и другими нормативными документами. Технические барьеры устанавливаются и обосновываются в проекте ядерной установки, радиационного источника и пункта хранения в соответствии с требованиями настоящего документа и других федеральных норм и правил в области использования атомной энергии.

6.3.1. Конструкция и конструкционные материалы ХЖО должны:

- предотвращать выход радионуклидов в окружающую среду выше пределов, установленных федеральными нормами и правилами в области использования атомной энергии;
- обеспечивать срок службы ХЖО не менее срока эксплуатации ядерной установки, радиационного источника и пункта хранения, на котором оно размещено.

Объем емкостей ХЖО должен обеспечивать необходимую технологическую выдержку ЖРО до их переработки и (или) распада короткоживущих радионуклидов.

6.3.2. Емкости для хранения ЖРО должны быть оснащены:

- трубопроводами и арматурой для приема ЖРО, направления их на кондиционирование, полного опорожнения;
- средствами контроля технологических параметров (температуры, давления, уровня в емкости), включая системы сигнализации о превышении верхнего уровня в емкости и контроля протечек ЖРО из емкости;
- радиационным контролем;
- пробоотборными устройствами, позволяющими производить отбор проб по всему объему емкости;
- устройствами для определения толщины (высоты) осадка;
- устройствами для диспергирования и удержания шлама (осадка) и отложений;
- оборудованием и трубопроводами для передачи растворов, шлама, сорбентов и смол из одной емкости в другую;
- трубопроводом перепада, соединенным с резервной емкостью, с диаметром большим, чем у приемного трубопровода;
- технологической службой под разрежением, связанной с системой технологических сдувок и предотвращающей образование повышенного давления в свободном объеме емкости;
- средствами контроля водорода, предупредительной и аварийной сигнализацией, автоматическими средствами пожарозащиты и при необходимости пожаротушения;
- устройствами, не допускающими повреждение емкости из-за повышения в них давления или их вакуумирования.

6.3.3. В емкостях для хранения ЖРО высокого уровня активности должны быть дополнительно предусмотрены технические методы и средства для предотвращения:

- разогрева и выпаривания ЖРО;
- накопления взрывоопасных газообразных веществ.

6.3.4. Конструкция емкости для хранения ЖРО должна позволять поиск мест протечек из емкости и выполнение ее ремонта.

6.3.5. Передача ЖРО из одной емкости для хранения ЖРО в другую должна осуществляться с использованием статического давления жидкости или газа (без применения насосов).

6.3.6. Помещения, предназначенные для размещения емкостей для хранения ЖРО, должны иметь не менее чем трехслойную гидронепроницаемую облицовку из нержавеющей стали. Объем облицованного помещения должен вмещать все количество ЖРО, находящегося в емкостях.

6.3.7. На территории вокруг помещений с емкостями для хранения ЖРО должны быть предусмотрены контрольно-наблюдательные скважины для отбора проб грунтовых вод. Количество и расположение наблюдательных скважин устанавливается в соответствии с нормативными документами.

6.3.8. В помещениях, в которых находятся емкости для хранения ЖРО, должны быть предусмотрены:

- сигнализация протечек из емкостей;
- система сбора и возврата протечек;
- вентиляция;
- радиационный контроль;
- средства для дезактивации.

6.3.9. Водно-химический режим в емкостях для хранения ЖРО должен исключать интенсивные коррозионные процессы.

6.3.10. Помещения, в которых находятся емкости с органическими ЖРО, должны быть снабжены устройствами пожарной сигнализации и средствами пожаротушения. Совместное хранение в помещениях органических ЖРО со средами, содержащими окислители, не допускается.

6.3.11. Проектом ядерной установки, радиационного источника и пункта хранения должны быть предусмотрены резервные емкости для хранения ЖРО, образовавшихся в результате аварий. Минимальный резервный объем емкостей для хранения ЖРО должен быть обоснован в проекте. На резервные емкости для хранения ЖРО и помещения, в которых они находятся, распространяются те же требования, что и на основные емкости для хранения ЖРО.

6.4. Хранение малых объемов ЖРО должно осуществляться в специально оборудованных помещениях. Расположение помещений, оборудование помещений для хранения малых объемов ЖРО и условия их хранения должны соответствовать требованиям Основных санитарных правил обеспечения радиационной безопасности (ОСРБ-99).

7. ТРЕБОВАНИЯ К ОБЕСПЕЧЕНИЮ БЕЗОПАСНОСТИ ПРИ ОТВЕРЖДЕНИИ ЖИДКИХ РАДИОАКТИВНЫХ ОТХОДОВ

7.1. Технологический процесс отверждения ЖРО должен обеспечивать получение продуктов с показателями качества, установленными в настоящем документе. Конкретные технические методы и средства отверждения ЖРО устанавливаются и обосновываются в проекте ядерной установки, радиационного источника и пункта хранения.

7.2. Отверждение ЖРО должно производиться методами цементирования, битумирования и остекловывания.

При выборе метода отверждения ЖРО должны учитываться:

- физические и химические характеристики ЖРО;
- свойства матричного материала;

предполагаемый способ хранения и (или) захоронения
кондиционированных отходов.

Допускается использование других методов отверждения ЖРО, разработанных в соответствии с достигнутым уровнем науки и техники.

7.3. Процесс отверждения ЖРО должен быть пожаро- и взрывобезопасным и не сопровождаться образованием значительного количества вторичных РАО.

7.4. При отверждении ЖРО методом цементирования должны выполняться следующие основные требования:

7.4.1. Установка цементирования должна находиться в отдельном помещении, снабженном системой вентиляции.

7.4.2. Используемые неорганические вяжущие (цемент, портландцемент, шлакопортландцемент и др.) должны обеспечивать качество цементной матрицы в соответствии с требованиями настоящего документа.

7.4.3. В цементную матрицу не могут включаться ЖРО, содержащие вещества, взаимодействующие с цементом с образованием токсичных веществ (например, соли аммония).

7.4.4. С целью предотвращения разлива в помещении цементного компаунда при его расфасовке в контейнеры должны быть предусмотрены:

- контроль размещения контейнера для цементного компаунда под сливным патрубком;
- контроль заполнения емкости цементным компаундом;
- устройство, исключающее возможность разлива во время транспортирования контейнера с цементным компаундом от места заполнения до места выдержки для отверждения.

7.4.5. Оборудование для перемешивания цементного теста с ЖРО должно обеспечивать получение гомогенного цементного компаунда с равномерным распределением радионуклидов по его объему.

7.4.6. При цементировании должно быть обеспечено управление технологическими параметрами процесса и контроль за ними, обеспечивающими получение цементного компаунда со следующими основными показателями качества:

Показатель качества	Допустимые значения
Удельная активность компаунда:	$< 3,7 \cdot 10^{10}$ Бк/кг ($1 \cdot 10^{-3}$ Ки/кг)
бета-активность	$< 3,7 \cdot 10^7$ Бк/кг ($1 \cdot 10^{-6}$ Ки/кг)
альфа-активность	
Водоустойчивость (скорость выщелачивания радионуклидов по Cs-137 и Sr-90)	$< 1 \cdot 10^{-3}$ г/см ² сут
Механическая прочность (предел прочности при сжатии)	≥ 50 кгс/см ²
Радиационная устойчивость	Механическая прочность не менее 50 кгс/см ² после облучения дозой 10^6 Гр (10^8 рад)
Устойчивость к термическим циклам	Механическая прочность не менее 50 кгс/см ² после 30 циклов замораживания и оттаивания (-40 ...

Водостойкость

+40 °C)

Механическая прочность не менее
50 кг/см² после 90-дневного
погружения в воду

Требования к методам контроля качества цементного компаунда устанавливаются нормативными документами.

7.5. При отверждении ЖРО методом битумирования должны выполняться следующие основные требования:

7.5.1. Установка битумирования должна находиться в отдельном помещении, снабженном системой вентиляции, пожарной сигнализацией и средствами пожаротушения.

7.5.2. Используемый в качестве матричного материала битум должен удовлетворять следующим основным требованиям:

- температура вспышки не ниже 200°C;
- температура воспламенения не ниже 250°C;
- температура самовоспламенения не ниже 400°C.

7.5.3. В битумную матрицу не должны включаться ЖРО, компоненты которых вступают с ней в химическое взаимодействие, сопровождающееся:

- экзотермическими эффектами;
- образованием токсичных или взрывоопасных веществ;
- ухудшением качества образующегося компаунда.

7.5.4. Солевые концентраты, направляемые на битумирование, должны удовлетворять следующим требованиям:

- концентрация сильных окислителей (нитраты трехвалентных металлов, марганцевокислый калий и т.п.) в ЖРО не должна превышать 5% от массы сухого остатка;
- содержание нитрата аммония в ЖРО не должно превышать 12% от массы сухого остатка;
- величина pH ЖРО должна находиться в пределах 6,5-11,5;
- удельная активность ЖРО не должна превышать $3,7 \cdot 10^{10}$ Бк/дм³ (1 Ки/дм³).

7.5.5. ЖРО не должны содержать органических веществ, которые в условиях проведения процесса битумирования могут образовывать легколетучие соединения в количествах, способных создать взрывоопасную концентрацию в газовой фазе. Должен быть обеспечен контроль за содержанием таких соединений в отходящих газах.

7.5.6. С целью предотвращения разлива в помещении битумного компаунда при его расфасовке должны быть предусмотрены:

- контроль размещения контейнера для битумного компаунда под сливным патрубком;
- контроль заполнения емкости битумным компаундом;
- устройство, исключающее возможность разлива во время транспортирования контейнера с битумным компаундом от места заполнения до места выдержки для остывания.

7.5.7. Параметры процесса битумирования должны обеспечивать получение однородного битумного компаунда с равномерным распределением его объема радионуклидов.

7.5.8. При битумировании должно быть обеспечено управление технологическими параметрами процесса и контроль за ними.

обеспечивающими получение битумного компаунда со следующими основными показателями качества:

Показатель качества	Допустимые значения
Удельная активность компаунда:	$< 3,7 \cdot 10^{10}$ Бк/кг ($1 \cdot 10^{-3}$ Ки/г)
бета-активность	$< 3,7 \cdot 10^7$ Бк/кг ($1 \cdot 10^{-6}$ Ки/г)
альфа-активность	
Водоустойчивость (скорость выщелачивания радионуклидов по Cs-137 и Sr-90)	$< 1 \cdot 10^{-3}$ г/см ² ·сут
Содержание свободной влаги в компаунде	$< 3 \%$
Термическая устойчивость	t° вспышки > 200 °C t° воспламенения > 250 °C; t° самовоспламенения > 400 °C
Радиационная устойчивость	Увеличение объема менее 10% после облучения дозой 10^4 Гр (10^5 рад)
Биологическая устойчивость	Отсутствие роста грибов

Требования к методам контроля качества битумного компаунда устанавливаются нормативными документами.

7.6. При отверждении ЖРО методом остекловывания должны выполняться следующие требования:

7.6.1. Установка остекловывания должна находиться в отдельном помещении, снабженном системой вентиляции.

7.6.2. С целью предотвращения разлива стеклоподобного материала при его расфасовке должны быть предусмотрены:

- контроль размещения контейнера для стеклоподобного материала под сливным патрубком;
- контроль заполнения емкости стеклоподобным материалом;
- устройство, исключающее возможность разлива во время транспортирования контейнера со стеклоподобным материалом от места его заполнения до места выдержки для остывания.

7.6.3. Концентрация плутония в ЖРО не должна превышать $0,03$ г/дм³.

7.6.4. При остекловывании должен быть обеспечен контроль концентраций радионуклидов и концентраций H₂, CO и других газов, отходящих из печи.

7.6.5. Химический состав ЖРО, используемые материалы и параметры процесса остекловывания должны обеспечивать получение однородного стеклоподобного материала с равномерным распределением по его объему радионуклидов.

7.6.6. При остекловывании должно быть обеспечено управление технологическими параметрами процесса и контроль за ними, обеспечивающими получение стеклоподобного материала со следующими основными показателями качества:

Показатель качества	Допустимые значения
Состав отвержденных ЖРО	<24 – 27% мас. Na_2O и оксидов одновалентных нуклидов; <20 – 24% мас. Al_2O_3 и оксидов многовалентных нуклидов, в том числе < 0,2% мас. трансурановых элементов; <50 – 52% мас. P_2O_5
Однородность	Равномерность состава блока по макрокомпонентам в пределах $\pm 10\%$; отсутствие выделения дисперсных фаз, особенно для альфа-излучателей. Количество альфа-излучателей < 0,2% мас.
Тепловыделение	< 5 кВт /м ³
Водоустойчивость (скорость выщелачиваемости радионуклидов по Cs^{137} , Sr^{90} , Pu)	10^{-5} - 10^{-6} г/см ² ·сут Cs^{137} ; 10^{-6} г/см ² ·сут Sr^{90} ; 10^{-7} г/см ² ·сут Pu
Термическая стойкость	Отсутствие изменений структуры и водостойкости в результате хранения при температуре до 450°C
Радиационная стойкость	Неизменность структуры и водостойкости при значениях: а) дозы – 10^6 Гр (10^{10} рад) (по β , γ -излучению), б) 10^{18} - 10^{19} α -распадов/см ³
Механическая прочность:	
Прочность на сжатие	(0,9 - 1,3) кгс/мм ² (0,9 - 1,3) · 10 ⁷ Н/м ²
Прочность на изгиб	(4,1 - 4,7) кгс/мм ² (4,1 - 4,7) · 10 ⁷ Н/м ²
Модуль Юнга	> 5400 кгс/мм ² (> 5,4 · 10 ¹⁰ Н/м ²)
Теплофизические константы:	
Коэффициент термического расширения	(8-15) · 10 ⁻⁶ 1/°C

Коэффициент теплопроводности	Изменения в пределах 0,7-1,6 Вт/м·К в интервале температур 20-500 °С
Газовыделение	Не допустимо

7.6.6. Требования к методам контроля качества стекломассы устанавливаются нормативными документами.

8. ТРЕБОВАНИЯ К ОБЕСПЕЧЕНИЮ БЕЗОПАСНОСТИ ПРИ КОНДИЦИОНИРОВАНИИ ЖИДКИХ РАДИОАКТИВНЫХ ОТХОДОВ

8.1. Кондиционирование ЖРО должно обеспечивать перевод ЖРО в формы, пригодные для последующего транспортирования, и (или) хранения, и (или) захоронения.

8.2. В зависимости от характеристик ЖРО и способов последующего обращения с кондиционированными ЖРО, в том числе их транспортирование, и (или) переработка, и (или) хранение, и (или) захоронение, кондиционирование ЖРО должно включать в себя одну из следующих операций или их совокупность:

- размещение ЖРО в контейнере;
- отверждение ЖРО и размещение отвержденных ЖРО в контейнере;
- размещение упаковки ЖРО в дополнительном контейнере.

8.3. В проекте ядерной установки, радиационного источника и пункта хранения должны быть обоснованы принятые в соответствии с требованиями настоящего документа, других федеральных норм и правил в области использования атомной энергии методы и средства кондиционирования ЖРО.

8.4. При установлении методов и средств кондиционирования ЖРО должны учитываться:

- характеристики ЖРО, подлежащих кондиционированию;
- способы последующего обращения с кондиционированными ЖРО, в том числе их переработка, и (или) транспортирование, и (или) хранение, и (или) захоронение;
- установленные для последующего обращения с ЖРО критерии качества.

8.5. Радионуклидный состав, удельная активность радионуклидов, суммарная величина активности в упаковке РАО, мощность эквивалентной дозы на поверхности контейнера, величина радиоактивного загрязнения наружной поверхности контейнера должны соответствовать критериям качества ЖРО для последующего этапа обращения с ними. Упаковка РАО должна предотвращать неприемлемое распространение радионуклидов в окружающую среду.

8.6. Упаковка кондиционированных РАО не должна содержать:

- сильных окислителей и химически неустойчивых веществ;
- коррозионно-активных веществ;
- ядовитых, патогенных и инфекционных веществ;

- биологически активных веществ;
- легковоспламеняющихся и взрыво- и пожароопасных веществ;
- веществ, способных к детонации или взрывному разложению;
- веществ, вступающих в экзотермическое взаимодействие с водой, сопровождающееся взрывом;
- веществ, содержащих или способных генерировать токсичные газы, пары или возгоны.

Содержание жидкости в упаковке РАО не должно превышать 3%.

8.7. Выбор конструкции контейнера и конструкционных материалов контейнера должен быть основан на:

- физических и химических характеристиках РАО;
- способах последующего обращения с упаковкой РАО;
- установленных для последующего обращения с РАО критериев качества.

8.8. Конструкция контейнера и конструкционные материалы контейнера должны обеспечивать сохранение его целостности и работоспособности, в том числе прочностных характеристик в период последующего обращения с упаковкой ЖРО.

8.9. Конструкционные материалы контейнера и использованные для покрытия его поверхностей материалы должны обеспечивать защиту от атмосферных воздействий и возможность проведения дезактивации.

8.10. При наличии в упаковке РАО коррозионно-активных веществ внутренние поверхности контейнера должны быть обработаны антикоррозионным покрытием.

8.11. Если проектом ядерной установки, радиационного источника и пункта хранения не установлены способ, место и конкретные сроки захоронения кондиционированных ЖРО, то используемый контейнер должен сохранять целостность в течение ожидаемого периода хранения до захоронения и предотвращать неприемлемое распространение радионуклидов из упаковки РАО.

Контейнер должен обеспечивать возможность:

- извлечения упаковки РАО из хранилища в конце периода хранения;
- размещения упаковки РАО в дополнительный контейнер при необходимости;
- транспортирования упаковки РАО на захоронение;
- обращения с упаковкой РАО при захоронении.

8.12. Если упаковка РАО не соответствует установленным критериям качества РАО для транспортирования, и (или) хранения, и (или) захоронения, то с целью исключения несоответствия должен быть использован дополнительный контейнер.

8.13. Контейнеры и упаковки РАО, предназначенные для долговременного хранения и (или) захоронения, подлежат обязательной сертификации.

8.14. Хранение кондиционированных ЖРО должно осуществляться в специально оборудованных хранилищах с системой барьеров, предотвращающей поступление радионуклидов в окружающую среду выше

пределах, установленных федеральными нормами и правилами в области использования атомной энергии. Технические характеристики барьеров, сроки хранения кондиционированных ЖРО и их количество устанавливаются и обосновываются в проекте ядерной установки, радиационного источника и пункта хранения в соответствии с требованиями настоящего документа и других федеральных норм и правил в области использования атомной энергии.

6.0 Attachment C

Collecting, Reprocessing, Storage, and Conditioning Liquid Radioactive Waste – Safety Requirements Presentation by V. A. Starchenko

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**Gosatomnadzor of Russia
Federal standards and regulations
in the field of use of nuclear power**

**Collecting, reprocessing, storage and conditioning
of liquid radioactive waste.
Safety requirements.**

НП-019-2000

**Put into effect
since January 1, 2001**

Purpose and area of application

The present document establishes requirements for ensuring safety when collecting, reprocessing, storing and conditioning LRW at nuclear facilities, radiation sources, and nuclear materials, radioactive substances and RW storages.

The present document doesn't apply to:

- treatment of LRW formed at production and enrichment of radioactive substances ores and other minerals;**
- handling of LRW accumulated in superficial reservoirs of nuclear fuel cycle objects.**

General safety requirements for collecting, reprocessing, conditioning and storing of radioactive waste

When establishing LRW quality criteria main characteristics of LRW, a container and LRW packing should be taken into account.

LRW characteristics:

- chemical composition and phase status;**
- total activity;**
- radionuclide composition, specific alpha and beta activity.**

Characteristics of solidified LRW:

Cement compound:

- radionuclide composition, specific alpha and beta activity, equivalent dose rate;**
- water resistance;**
- mechanical strength;**
- radiation stability;**
- thermal stability.**

LRW container characteristics:

- corrosion stability, radiation stability, configuration – for a metal container;
- density, porosity, water permeability, gas permeability, resistance to cold, radiation stability, resistance to microbes, mold and fungi, resistance to fire – for a ferroconcrete container.

LRW packing characteristics:

- radionuclide composition, alpha and beta activity, equivalent dose rate;
- total activity;
- homogeneity;
- mechanical strength (static, dynamic, impact loads);
- resistance to heat loads and thermal cycles;
- radiation stability.

When collecting, reprocessing, storing and conditioning of LRW the following potentialities should be excluded:

- uncontrollable change of LRW state of aggregation, including formation of deposits and sediments;**
- uncontrollable occurrence of exothermic reactions;**
- uncontrollable formation of corrosive substances.**

At collecting, reprocessing, storing and conditioning of LRW containing nuclear hazardous fission materials the opportunity of a self-supporting chain reaction occurrence.

Collecting, reprocessing, storing and conditioning of LRW together with not radioactive waste are not authorized.

Safety requirements for liquid radioactive waste collecting

LRW collecting should be carried out separately depending on the following:

- radionuclides half-life period (less than 15 days, more than 15 days);**
- specific activity;**
- concentration of alpha active radionuclides;**
- chemical composition;**
- phase composition;**
- prospective reprocessing method.**

Organic dangerously explosive and fire hazardous LRW should be collected separately from other types of LRW.

Safety requirements to liquid radioactive waste reprocessing

LRW reprocessing should provide purification of LRW liquid phase and radionuclides concentrating in smaller volume.

Complete dehydration of high-salt aqueous LRW solutions is not allowed in the case of possible exothermic interaction of components of the LRW dry residue.

Safety requirements for liquid radioactive waste storing

Premises intended for accommodation of capacities for LRW storing should have not less than three-layer waterproofing and facing from corrosion-proof steel. Volume of the reveted premise should contain all amount of LRW taking place in capacities.

Control and observation chinks for earth waters sampling should be stipulated in the territory around of premises with capacities for LRW storing.

Premises in which there are capacities for LRW storing should be provided with:

- leak alarm;**
- leaks collection and recovery system;**
- ventilation;**
- radiation control;**
- means for decontamination.**

- cement compound should have the following parameters of quality:

Quality parameter	Allowable values
Specific activity of compound	$< 3,7 \cdot 10^{10}$ Bq/kg ($1 \cdot 10^{-3}$ Ci/g)
Beta activity	$< 3,7 \cdot 10^7$ Bq/kg ($1 \cdot 10^{-6}$ Ci/g)
Water resistance (leaching rate for cesium-137 and strontium-90)	$< 1 \cdot 10^{-3}$ g/cm ² day
Mechanical strength (compression strength)	≥ 50 kg-force/cm ²
Radiation stability	Mechanical strength not less than 50 kg-force/cm ² after irradiation by the dose of 10^6 Gy (10^8 rad)
Resistance to thermal cycles	Mechanical strength not less than 50 kg-force/cm ² after 30 cycles of freezing and defrosting (-40 - +40 °C)
Water resistance	Mechanical strength not less than 50 kg-force/cm ² after 90-day immersion in water

Safety requirements for liquid radioactive waste solidification

The technological process of LRW solidification should provide reception of products with quality parameters established in the present document. Specific technical methods and means for LRW solidification are established and proved in nuclear facility, radiation source and storage designs.

The LRW solidification process should be fire- and explosion-proof and not be followed by formation of significant amount of secondary radioactive waste.

During LRW solidification using the method of cementation the following basic requirements should be carried out:

- the cementation facility should be in a separate premise supplied with ventilation system;**
- the used inorganic binders (cement, Portland cement, slag Portland cement and others) should provide quality of a cement matrix according the requirements of the present document;**
- LRW containing substances cooperating with cement with formation of toxic substances (for example, ammonium salts) can not be included in a cement matrix;**

Safety requirements for liquid radioactive waste conditioning

LRW conditioning should provide LRW reduction into forms suitable for the subsequent transportation, storing and (or) burial.

Conditioned radioactive waste package should be free of:

- strong oxidizers and chemically unstable substances;**
- corrosive substances;**
- poisonous, pathogenic and infectious substances;**
- biologically active substances;**
- highly inflammable, dangerously explosive and fire hazardous substances;**
- substances entering in exothermic interaction with water followed by explosion;**
- substances containing or capable to generate toxic gases, fumes or sublimates;**
- liquid contents in the radioactive waste package should not exceed 3%.**

Radioactive waste containers and packages intended for long-term storing and (or) burial are subject for obligatory certification.

Distribution:

Adkins, B. J., 742-7G
Argyle, M. D., INEEL
Butcher, B. T., 773-43A
Callison, S., CH2M Hill
Cammann, J. W., CH2M Hill
Carteret, B., PNNL
Chapman, N. F., 703-H
Cruz, J., DOE-ORP
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Lockie, K., DOE-ID
Martin, B. A., 742-4G
Nickola, C., PNNL
Rinker, M., PNNL
Stevens, W. E., 773A
Suggs, P. C., 704-3N
Taylor, P., ORNL
Thomas, J. L., 742-4G
Westsik, J., PNNL
Williams, B., PNNL
WPT File (2)
ORNL File (4)
TFA (4)
STI (4), 703-43A

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